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Portable Miniature Sampler for Potential Airborne Carcinogens in Microenvironments Phase 2. Evaluation

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PORTABLE MINIATURE SAMPLER FOR POTENTIAL AIRBORNE CARCINOGENS IN MICROENVIRONMENTS

Phase 2. Evaluation

by
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Contract No. 68-02-2774

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16. ABSTRACT

A portable sampling system was developed for the collection and concentration of a broad range of organic compounds from ambient air. The system is based on the use of three solid sorbent materials (Tenax-GC, Porapak R, and Ambersorb XE-340 arranged in series) through which air is drawn by a portable battery-powered pump. Two different portable pumps (DuPont P4000 and Spectrex PAS 3000) were used to power the portable sampling device in field evaluations of the system.

The system was evaluated in field studies conducted in Dayton, Ohio; Los Angeles, California; Houston, Texas; Niagara Falls, New York; Research Triangle Park, North Carolina; and Cincinnati, Ohio. Both indoor and outdoor environments were included among those sampled. Analyses were conducted for selected target compounds as well as additional broad-scan quantitative analysis of collected organic compounds. Analyses of the samples were accomplished using thermal desorption of the sorbent materials followed by capillary column gas chromatography/mass spectrometry. Partial pre-analysis fractionation (based primarily on volatility) was obtained in some of the sampling applications demonstrating that in certain environments additional capacity beyond that of Tenax-GC may be required to sample low level organic atmospheric pollutants.

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ABSTRACT

A portable sampling system was developed for the collection and concentration of a broad range of organic compounds from ambient air. The system is based on the use of three solid sorbent materials (Tenax-GC, Porapak R, and Ambersorb XE-340 arranged in series) through which air is drawn by a portable battery-powered pump. Two different portable pumps (DuPont P4000 and Spectrex PAS 3000) were used to power the portable sampling device. Generally. 250 to 500 L of air were sampled with this system in an eight hour period. Analyses of the samples were accomplished using thermal desorption of the sorbent materials followed by capillary column gas chromatography/mass spectrometry. Analyses were conducted for selected target compounds as well as additional broad-scan qualitative analysis of all of the collected organic compounds.

The system was evaluated by field studies conducted at six locations. Analysis of samples collected at Niagara Falls and Research Triangle Park (both indoor) found all of the collected organic compounds on the Tenax in the first collection tube. Samples collected in Houston (outdoor) had compounds on both the Tenax and Porapak tubes, while samples collected in Dayton (outdoor), Los Angelas (outdoor), and Cincinnati (indoor) had organic compounds on Tenax, Porapak, and Ambersorb tubes. In no case was anything other than carbon dioxide found on the back-up Ambersorb tube.

When organic compounds were found on more than one tube, the highest molecular weight (lowest volatility) compounds were found on the Tenax, intermediate compounds on the Porapak, and the most volatile compounds on the Ambersorb. This multiple sorbent portable sampling system weighs less than five pounds. It has been found to collect for analysis a wide range of organic compounds from ambient air under a variety of environmental conditions.

CONTENTS

Abstract iii
Figures vi
Tables ix
Acknowledgement xii
1. Introduction 1
2. Conclusions 2
3. Recommendations 4
4. Program Overview 5
    Objective 5
    Program 5
5. Review of Sampling and Analytical Techniques and Compilation of Pertinent Data 7
    Objective 7
    Instrumentation 7
    Review 7
    Discussion 8
6. Development of The Analytical Method 22
    Objective 22
    Instrumentation 22
    Evaluation 22
    Results 48
7. Development of The Sampling System 51
    Objective 51
    Instrumentation 51
    Evaluation 51
    Results 75
    Discussion 80
8. Collection of Field Samples 82
    Objective 82
    Instrumentation 82
    Field Sampling 82
9. Analysis of Field Samples by Capillary Gas Chromatography/Mass Spectrometry 98
    Objective 98
    Instrumentation 98
    Evaluation 98
    Results 100
References 129
Appendices

A. Operation Manual 134
B. Standard Sample Generation System 191

Preceding page blank

FIGURES

Number Page

1 Program outline for EPA Contract No. 68-02-2774. . 6

2 Chromatogram of column test mixture IIb. 27

3 Chromatogram of column test mixture IIIa 28

4 Van Deemter plot for analytical column 32

5 Effect of oven temperature on flow rates and linear velocity. 33

6 Typical chromatogram of Standard Mixture $(GC)^2$Va . 34

7 Chromatograms of Standard Mixture $(GC)^2$Va. 35

8 Flow schematic of capillary inlet system 37

9 Schematic of flow pattern at the capillary GC injection port 38

10 Front and rear view photograph of new, durable capillary inlet system desorption chamber. . . . 40

11 Sketch of capillary inlet system thermal control unit 41

12 Capillary GC with capillary inlet system 42

13 Comparison of trap designs and their temperature zones during cryogenic sample reconcentration. . 43

14 Injection system with modified septum tee. 47

15 Chromatograms of Standard Mixture $(GC)^2$Va comparing split and splitless modes of injection . . . 49

16 Basic sampling system. 52

17 Sketch and description of small personnel sampler. 53

FIGURES (continued)

Number		Page
18	Sketch and description of large desk-top sampler	54
19	Relationship between concentration, volume sampled, and approximate detection limit (10 ng) for benzene with sorbent capacities superimposed (assuming 1 gram of sorbent)	58
20	Plots of requirements for various sampling arrangements and the manufacturer's specifications for four miniature pumps	62
21	Plots of requirements for various sampling arrangements and the manufacturer's specifications for two large (desk-top) pumps	63
22	Specifications of selected sampling tube design	63
23	Backgrounds produced by desorbing blank sorbent tubes	67
24	Comparison of "frontal" and "elution" methods of sorbent capacity determination	68
25	"Pass-through" solvent desorption technique	71
26	Solvent "bath" desorption technique	71
27	"Breadboarded" version of the portable miniature sampling system with sorbent tubes in series	76
28	Schematic of the "Breadboarded" version of the sampling system with the sorbent tubes in parallel	77
29	The "tube tray" portion of the Ambient Air Collection System	78
30	Portable Miniature Collection System	79
31	Theoretical performance of multi-residue sampling system	81
32	Locations of high ground level concentrations - Los Angeles, California	89
33	Locations of maximum concentration of pollutants in Houston	94

FIGURES (continued)

Number		Page
34	Reconstructed total ion chromatogram of Tenax Collector Sample from Dayton Sampling.	104
35	Reconstructed total ion chromatogram of materials collected in metropolitan Los Angeles by the multisorbent air sampling technique.	105
36	Qualitative scan of a Tenax collector sample from Niagara Falls sampling with the Portable Miniature System	108
37	Reconstructed total ion chromatogram of compounds collected in Houston on Tenax-GC using the portable miniature collection system	111
38	Reconstructed total ion chromatogram of materials collected on Porapak R collector in Houston, Texas.	112
39	Reconstructed total ion chromatogram of Public Health Inititive Compounds - 200 mg each	117
40	Reconstructed total-ion chromatogram of Personnel Monitoring Sample collected in Cincinnati, Tenax collector.	124
41	Reconstructed total-ion chromatogram of Porapak collector contents, Cincinnati sampling.	126
42	Reconstructed total-ion chromatogram of First Ambersorb collector contents, Cincinnati sampling	127

TABLES

Number		Page
1	Twenty Selected Target Compounds for Portable Sampler Evaluation	8
2	Pertinent Information for the Selected Compounds .	9
3	Hazardous Properties of Selected Compounds	13
4	Mass Spectral Information for Selected Compounds .	15
5	Directory of Information Contained in Literature References	17
6	Concentrations of Various Compounds in Air Samples Reported in Literature References.	20
7	Chromatographic Properties of the Twenty Selected Compounds on Various Capillary Columns	24
8	Composition of Column Text Mixture IIb	26
9	Composition of Column Test Mixture IIIa.	26
10	Chromatographic Performance of Various Capillary Columns.	30
11	Effect of Capillary Inlet System on the Chromatographic Performance of Various Capillary Columns.	46
12	Reproducibility of Retention Times	47
13	Reproducibility of Area Integrations	47
14	Adsorbent Properties Chart	56
15	Evaluation of Sorbent Package for Two Modes. . . .	57
16	Results of Pressure Drop Studies Across Two Diameters of Tapered Glass Sampling Tubes. . . .	60
17	Total Pressure Drops Across Different Sampling Configurations	61

TABLES (continued)

Number		Page
18	Summary of Anticipated Sampling Characteristics and Capabilities	65
19	Results of Frontal Analyses of Sorbent Tubes	70
20	Evaluation of the Desorption Efficiency of Benzene from Ambersorb XE-340	72
21	Recovery of Standards from Sorbent Tubes	73
22	Percent Recoveries of Theoretical Amounts of Generated Samples	74
23	Percent Recoveries of Selected Amounts of Generated Samples	74
24	Sampling Plant - Dayton	84
25	Sampling Conditions - Dayton	85
26	Sampling Plan - Los Angeles	86
27	Field Spiking Solution A	87
28	Field Spiking Solution B	87
29	Field Spiking Solution C	87
30	Field Spiking Solution E	88
31	Field Spiking Solution F	88
32	Los Angeles - Potential Carcinogenic Composition at Points of Maximum Concentration (micrograms per cubic meter)	88
33	Sampling Conditions - Los Angeles	90
34	Sampling Plan - Niagara Falls	91
35	Sampling Conditions - Niagara Falls	92
36	Sampling Plan - Houston	93
37	Average Concentrations at Points of Maximum Pollution in Houston (micrograms per cubic meter)	95

TABLES (continued)

Number Page

38 Sampling Conditions - Houston. 96

39 RTP and Cincinnati Target Compounds. 96

40 RTI Sampling Data. 97

41 Compounds Detected in Ambient Air Samples Collected in Dayton. 103

42 Subject Compounds Present in Samples Collected in Metropolitan Los Angeles 106

43 Compounds Detected in Ambient Air Samples Collected in Indoors at Niagara Falls, NY. 109

44 Subject Compounds Detected in Samples Collected Indoors at Niagara Falls 110

45 Compounds Collected on Tenax During Houston Sampling 113

46 Compounds Detected in Ambient Air Samples Collected at Houston Porpak R Collector. 114

47 Subject Compounds Present in Samples Collected in Houston, Texas 115

48 Public Health Inititive Compounds. 116

49 Evaluation of Calibration Data 118

50 Analysis of Spike Set #1 119

51 Analysis of RTI Spike Set #2 120

52 Target Compounds Collected at RTP During Personnel Monitoring of EPA Employee 121

53 Additional Compounds Detected in RTP Personnel Monitor Samples. 122

54 Target Compounds Collected at Cincinnati During Personnel Monitoring of MRC Employee 123

55 Major Components Detected in Personnel Monitoring Sample Collected in Cincinnati 125

56 Compounds Detected in Second and Third Sorbent Tubes During Sampling in Cincinnati. 128

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SECTION 1

INTRODUCTION

The general population, particularly in urban areas, is exposed to a wide variety of atmospheric pollutants. The health hazard posed by this situation cannot currently be adequately defined because of the complexity of the problem and the lack of sufficient, reliable data. One of the needs in assessing this exposure problem is a reliable screening technique for determining what substances at what concentrations are present in our ambient atmosphere.

The ability to assess the extent of a health hazard in ambient air requires at least three things:

(1) Knowledge of the materials that pose the hazard,

(2) A reliable sampling technique for collecting these materials, and

(3) Adequate technology for accurate analyses of these materials.

The objective of this research program was to develop a portable miniature collection system that could be used to assess the exposure of an individual to atmospheric pollutants, especially those pollutants that potentially threaten the health of the individual. Since a wide variety of gases, vapors and particulates of organic compounds, ranging from volatile hydrocarbons (e.g., methane) to high molecular weight phthalates (plasticizers), polychlorinated biphenyls pesticides, and polynuclear aromatics, are present as pollutants within the atmosphere, the collection system was to be capable of concentrating a wide variety of organic compound vapors from ambient air. A number of organic compounds suspected of being carcinogens, mutagens, cofactors, or precursors, and therefore of environmental and health concern, was to be selected for specific evaluation.

The result of this research is a sampling system and associated analytical methodology that is capable of screening for a broad range of organic components in ambient air and in particular for assessing the presence/absence of the selected potential carcinogenic compounds. This represents a step toward a reliable approach for assessing the health hazard of an individual posed by potentially carcinogenic materials in ambient air.

TODAY

GRADUATE SEMINARS ON THE ENVIRONMENT

UNIVERSITY OF CINCINNATI-ENVIRONMENTAL RESEARCH CENTER, USEPA

THURSDAY, OCTOBER 15

12:30 PM

POLITICS AND THE ENVIRONMENT

Thomas B. Brush
Vice-Mayor
City of Cincinnati

Auditorium

Environmental Research Center, USEPA

OPEN TO ALL EMPLOYEES

OPEN TO THE PUBLIC

Synopsis

Over the years, the City of Cincinnati and the county in which it resides have had environmental problems with the air their citizens breathe and with the water they drink. And, ever present is the statistic that the county suffers one of the highest cancer death rates in the nation.

Thomas B. Brush, Vice-Mayor of Cincinnati, will discuss the legislative role in protecting the environment for the public.

SECTION 2

CONCLUSIONS

A three-sorbent, portable, sample collection system was designed, evaluated, and field tested in Dayton, Los Angeles, Niagara Falls, Houston, Research Triangle Park (RTP) and Cincinnati. The sorbents were operated in series drawing air in turn through Tenax GC, Porapak R, and Ambersorb XE-340 using a small personal pump. This selection of sorbent materials was judged the best combination of commercially available sorbents for broad-range organics sampling. Two types of small personal pumps, DuPont Model P-4000 and Spectrex Model PAS-3000, were used to collect samples during these field evaluations.

In terms of concentrating organic compounds on the sorbent materials, the portable sampling system operated as anticipated in field sampling applications. The need for additional, complementary sorbent capabilities to those of Tenax was demonstrated in the Los Angeles and Houston samples where significant amounts of organics were observed on the subsequent (Porapak and Ambersorb) tubes. A partial fractionation was also observed on the various sorbent materials where different ranges of compounds (based primarily on volatility) were found. There appears to be some influence exerted by matrix and/or humidity effects on the amount of breakthrough that is observed on the latter sorbents. The Niagara Falls and RTP samples were collected in an interior environment and exhibited little if any compound breakthrough to the Porapak and Ambersorb materials. The Cincinnati sample was collected primarily in an indoor atmosphere except for the time in route from Dayton to Cincinnati by automobile. Unlike the RTP and Niagara Falls samples, some sample breakthrough past the Tenax tube was observed.

The original design of the system used a DuPont Model P-4000 pump. However, the considerable pressure drop (75-100 mm of Hg) across the sorbent collection tubes assembled for the normal series operation proved to be too high for reliable pump operation under the desired conditions (i.e., up to 1 L/min flow for 8 hours). A higher capacity portable pump (Spectrex Model PAS-3000) and larger diameter tubes (producing only 30-40 mm of Hg pressure drop) were incorporated into the final design to achieve more reliable operation. This system was used on the RTP and Cincinnati sampling trips.

The number of compounds from the list of target compounds observed in actual field samples was small. The largest number and highest concentrations were observed in the Niagara Falls samples.

The analytical methodology was based primarily on capillary column GC/MS using thermal desorption for recovering the sample from the sorbents for analysis. Samples collected in high humidity environments (e.g., Houston) caused particular problems in the analysis phase due to high concentrations of water collected on the Porapak and Ambersorb sorbents. However, it was found that by changing certain analytical parameters (e.g., initial GC temperature), a satisfactory analysis could be performed in these instances.

SECTION 3

RECOMMENDATIONS

The following recommendations are made as the result of the research conducted on this program:

(1) The sampling system that was developed should be extensively evaluated in other field sampling situations to further define its operational capabilities.

(2) The technique should be used primarily as a "screen" for the presence/absence of specific compounds or for wide-scan evaluation of organic composition in ambient air much as the EPA Priority Pollutant Protocol is used as a "screen" for organics in industrial effluents.

(3) Only after the system has been validated for a specific compound(s) in a particular air matrix should it be used to generate quantitative data.

(4) Validation should consist of the use of spikes to determine actual recoveries of the compounds of interest. Stable isotopically labelled compounds should be used where possible to allow differentiation between the spike and the native compound.

(5) When a compound of concern is identified through the screening process, careful consideration and confirming studies should be made to determine if this compound is real or an artifact of the sampling/analytical techniques.

SECTION 4

PROGRAM OVERVIEW

OBJECTIVE

The objective of this research program was to develop a portable miniature collection system that could be used to assess the exposure of an individual to a wide variety of atmospheric pollutants some of which present potential health hazards. Of particular interest were organic compounds suspected of being carcinogens, mutagens, cofactors, or precursors. Twenty compounds were selected for specific assessment to evaluate the capabilities of the sampling technique. An analytical technique using capillary chromatography/mass spectrometry was also developed.

PROGRAM

The program that was developed to address this objective was divided into four phases that roughly paralleled the three years of the contract (outlined in Figure 1). Phase 1 dealt with the selection of candidate sorbent materials; the selection of test compounds for sorbent evaluation; the evaluation of the sorbent materials in terms of capacity, desorption properties, and physical properties that relate to pressure drops and ultimate system design; the selection of a three-sorbent system based on Tenax-GC, Porapak R, and Ambersorb XE-340; and the consideration of various design parameters for the pump and system hardware. The results of the activities of Phase 1, along with some initial analytical method development, were reported in a separate report [1].

The second phase of this program dealt with the selection of compounds for specific consideration, the development of methodology for the analysis of collected samples, and the evaluation and refinement of the analytical technique. The results of the first phase of a companion program (EPA Contract No. 68-02-2773) were used for the selection of the compounds considered in this

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[1] Brooks, J. J., and D. S. West. Portable Miniature Sampler for Potential Airborne Carcinogens in Microenvironments, Phase 1: Development. EPA-600/2-80-026, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, February 1980. 91 pp.

Phase 1	· Select at least 3 sorbents for evaluation
	· Establish matrix of test compounds
	· Evaluate candidate sorbents
	· Design portable cartridges collection system
Phase 2	· Evaluate sampling system for collection efficiency, stability, selectivity, desorption efficiency, etc., including analysis by GC/MS
Phase 3	· Test sampling and analysis methodology in selected urban areas
Phase 4	· Deliver test systems to EPA

Figure 1. Program outline for EPA Contract No. 68-02-2774.

program. Under the companion program atmospheric pollutants, were evaluated for importance as pollutants in terms of quantities emitted, persistance, and potential carcinogenicity. In addition, a review of the carcinogen cofactor literature was conducted, and isopleths for potential sampling sites were generated using the MRC Source Assessment Data Base and the EPA Climatological Dispersion Model. These results of these activities have also been previously reported [2]. The 20 compounds selected were further evaluated for use in this program, as discussed in Section 5. Sections 6 and 7 present the work performed to evaluate and refine the sampling technique and to develop the analytical method.

The third phase of the program involved the field evaluation of the system in Dayton, Los Angeles, Niagara Falls, Houston, Research Triangle Park, and Cincinnati using the sampling system developed on this program. The results from the sampling and subsequent analyses are discussed in Sections 8-9.

The fourth phase of this program will be completed with the delivery of the portable sampling systems to the EPA, along with the operation manual provided in Appendix A of this report.

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[2] McMillin, C. R., L. B. Mote, and D. G. DeAngelis. Potential Atmospheric Carcinogens, Phase 1: Identification and Classification. EPA-600/2-80-015, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, January 1980. 253 pp.

SECTION 5

REVIEW OF SAMPLING AND ANALYTICAL TECHNIQUES AND COMPILATION OF PERTINENT DATA

OBJECTIVE

A brief literature survey was conducted (in part under EPA Contract No. 68-02-2773) to acquire information on the twenty selected potential carcinogens to be evaluated in this program (see Table 1). This information was to be used for developing a means of quantitatively determining these selected, atmospheric pollutants.

INSTRUMENTATION

Information on exisiting sampling applications for the twenty selected compounds was obtained by using MRC's Information Retrieval System. The system provided access to bibliographic citations in 240 data bases through a Texas Instrument's Inc., Silent 700 electronic data terminal. By entering carefully selected combinations of key words, bibliographies were obtained of journal articles, government reports, patents, books, and ongoing research projects pertaining to the subject of interest. Citations of particular interest were noted. Complete copies of these citations (articles, books, etc.) were obtained from MRC's technical library.

REVIEW

Information was acquired for practical laboratory use concerning:

- Pertinent physical properties (Table 2),
- Hazards and proper handling practices (Table 3),
- Mass spectral characteristics (Table 4), and
- Environmental and occupational sampling applications.

In addition to basic properties and handling procedures for these compounds, insight was sought into the problems and potential problems associated with sampling and analyzing these potential carcinogens.

TABLE 1. TWENTY SELECTED TARGET COMPOUNDS FOR PORTABLE SAMPLER EVALUATION

Acrolein	1,4 Dioxane
Acrylonitrile	Ethylene dibromide
Benzene	Ethylene dichloride
Benzidine	Ethylene oxide
Benzo(a)pyrene	Hexachloro-1,3-butadiene
Benzyl chloride	Pentachlorophenol
Carbon tetrachloride	Styrene
Chrysene	Tetrachloroethylene
1,3-Dichloropropene	Toluene-2,4-diamine
Di-(2-ethylhexyl)phthalate	Vinyl Acetate

The literature on sampling applications was obtained using MRC's Information Retrieval System (previously described), while information on physical characteristics, hazardous properties, and mass spectra was obtained from common reference materials. Most of the literature on sampling applications discussed specific sampling and analytical procedures for one or a few compounds, usually in ambient or workplace air. A few references gave a review of previous literature and an overview of techniques available for a specific compound. A few others evaluated methodologies used in laboratory validations, statistical treatments of data, laboratory handling of hazardous chemicals, and relevant sampling programs. Basic research into sorbent characteristics, sampling phenomena, etc., were also discussed in a few references. A directory of the information available in these articles is given in Table 5. The values reported in these references for the concentrations of various compounds found in air samples are compiled in Table 6.

DISCUSSION

The literature review sampling applications revealed that a wide variety of techniques and methods are available for obtaining and evaluating air samples. Unfortunately, many of these sampling and analytical techniques are not applicable to the simultaneous determination of compounds varying widely in volatility and functionality. For example, glass filters can be used to obtain high-volume particulate samples containing organic compounds such as benzo(a)-pyrene. Volatile compounds such as carbon tetrachloride, however, are not collected by this technique.

For this project the sampling technique of interest for the collection of the twenty selected compounds was adsorption on solid sorbent materials. More specifically, this project was to address the use of a combination of solid sorbents, complimentary

TABLE 2. PERTINENT INFORMATION FOR THE SELECTED COMPOUNDS

Compound information [3]				Physical properties [3]				
Name	Synonyms	Structure	CAS. No. [6]	M.W., g/mol	Den, g/mL	M.P., °C	B.P., °C	Vap. P., Pa (mm Hg)
1. Acrolein	Acrylaldehyde, propenal, acrylic aldehyde	CH_2=CHCHO	107-02-8	56.06	0.841	-87.7	52.5	2.9×10^4, (220) @20°C
2. Acrylonitrile	Propenenitrile, vinyl cyanide	CH_2=CHCN	107-13-1	53.06	0.797 0.806	-82	78-9	1.3×10^4, (100) @23°C
3. Benzene	Benzol, benzole, phene	C_6H_6	71-43-2	78.11	0.879	5.5	80.1	1.0×10^4, (76) @20°C
4. Benzidine	p,p'-bianiline, 4,4'-diaminobiphenyl	$NH_2C_6H_4$-$C_6H_4NH_2$	92-87-5	184.2	1.250	116-130	401.7 subl.	--
5. Benzo(a)pyrene	1,4-benzopyrene	$C_{20}H_{12}$	50-32-8	252.3	--	177	312@ 1.3×10^3 Pa, (10 mm Hg)	--
6. Benzyl chloride	α-chlorotoluene	C_6H_5-CH_2Cl	100-44-7	126.6	1.103	-43	179	130, (1) @22°C
7. Carbon tetrachloride	Tetrachloromethane	CCl_4	56-23-5	153.8	1.595	-23	76.8	1.2×10^4, (90) @20°C
8. Chrysene	Benzo(a)phenanthrene	$C_{18}H_{12}$	218-01-9	228.3	--	255-6	448	--
Cumene hydroperoxide	Dimethylbenzylhydroperoxide	C_6H_5-$C(CH_3)_2$-OOH	80-15-9	~152	--	--	153	130, (1) @70°C
9. Di-(2-ethylhexyl) phthalate (DEHP)	Dioctyl phthalate (DOP)	C_6H_4-$[CO_2CH_2$-$(C_2H_5)C_4H_9]_2$	117-81-7	390.6	0.986	-55	385	160, (1.2) @200°C
10. 1,4-Dioxane	(1,4) diethylene dioxide, glycol ethylene ether	$OC_2H_4OC_2H_4$	123-91-1	88.12	1.034	11.8	101	4.0×10^3, (30) @20°C

(continued)

TABLE 2 (continued)

Compound information [3]				Physical properties [3]				
Name	Synonyms	Structure	CAS. No. [6]	M.W., g/mol	Den, g/mL	M.P., °C	B.P., °C	Vap. P., Pa (mm Hg)
11. Ethylene dichloride	1,2-dichloroethane	$ClCH_2CH_2Cl$	107-06-2	96.96	1.257	-35.4	83.5	8.1×10^3, (61) @20°C
12. Ethylene oxide	1,2-epoxyethane, oxirane	CH_2CH_2O	75-21-8	44.05	0.882	-111	10.7	1.5×10^5, (1095) @20°C
13. Hexachloro-1,3-butadiene	--	$CCl_2=CCl-$ $CCl=CCl_2$	87-68-3	260.8	1.682	-21	215	2.9×10^3, (22) @100°C
14. Pentachlorophenol	--	Cl_5C_6OH	87-86-5	266.4	1.978	191	310 decom.	1.4×10^{-2}, (1.1×10^{-4}) @20°C
15. Styrene	Vinyl benzene, phenyl ethylene, cinnamate	$C_6H_5CH=CH_2$	100-42-5	104.16	0.907	31	146	670, (5) @20°C
16. Tetrachloroethylene	Perchloroethylene	$CCl_2=CCl_2$	127-18-4	165.83	1.505	-22.4	121.0	1.9×10^3, (14) @20°C
Tetraethyl lead	--	$Pb(C_2H_5)_4$	78-00-2	323.5	1.659	--	198.2	20, (0.15) @20°C
17. Toluene-2,4-diamine	4,m-tolylene-diamine, 2,4-diaminotoluene, 2,4-toluylene-diamine	$CH_3C_6H_3(NH_2)_2$	95-80-7	122.2	--	99	280	130, (1) @106.5°C
18. Vinyl acetate	Acetic acid, ethenyl ester	$CH_3CO_2CH=CH_2$	108-05-4	86.09	0.932	-93.2	72.2	1.1×10^4 (83) @20°C
19. Ethylene dibromide	1,2-dibromomethane	$Br_2CH_2CH_2Br$	106-93-4	187.9	2.170	9.8	131.4	--
20. 1,3-Dichloropropene	(cis) (trans)	$ClCH_2CH=CHCl$	542-75-6	111.0 111.0	1.473 1.468	-- --	104.3 112	-- --

(continued)

TABLE 2 (continued)

		Solubility parameter [4,5]				Pollutant information [2]			
		δ Calc^a [4]	Calc Sm^b	Lit Sm^b	δ Lit^a [5]	Carcinogen	Emissions, kg^c	Half life, da	Priority,^{d} kg
1.	Acrolein	10.0	560	--	--	Possible	1.1×10^4	0.11	6.4×10^1
2.	Acrylonitrile	10.8	573	557	10.5	Probable	3.7×10^5	--	1.7×10^2
3.	Benzene	9.2	719	719	9.2	Probable	5.9×10^7	3	3.4×10^5
4.	Benzidine	--	--	--	--	Probable	3.5×10^4	1	4.8×10^1
5.	Benzo(a)pyrene	--	--	--	--	Probable	8.3×10^5	--	8.3×10^5
6.	Benzyl chloride	9.9	1253	--	--	Probable	4.1×10^5	--	3.4×10^2
7.	Carbon tetrachloride	9.4	1447	1323	8.6	Probable	1.6×10^7	70-230	9.3×10^4
8.	Chrysene	--	-	--	--	Probable	1.7×10^4	--	6.1×10^2
	Cumene hydroperoxide	--	--	--	--	Possible	8.2×10^4	<0.2	4.8×10^2
9.	Di-(2-ethylhexyl) phthalate (DEHP)	--	--	--	--	Possible	1.2×10^6	1	7.0×10^3
10.	1,4-Dioxane	10.9	956	881	9.9	Probable	1.3×10^6	0.40	7.5×10^3
11.	Ethylene dichloride	10.4	1013	--	--	Probable	9.1×10^7	10-1000	1.1×10^5
12.	Ethylene oxide	15.0	660	489	11.1	Possible	3.8×10^4	0.13	2.2×10^2
13.	Hexachloro-1,3-butadiene	10.4	2783	--	--	Possible	3.4×10^6	<1	2.0×10^4
14.	Pentachlorophenol	--	--	--	--	Possible	2.1×10^7	>72	5.4×10^4
15.	Styrene	9.0	940	969	9.3	Possible	5.6×10^6	--	3.2×10^4
16.	Tetrachloroethylene	10.6	1758	1542	9.3	Probable	8.5×10^7	2-8	4.9×10^5
	Tetraethyl lead	--	--	--	--	Possible	4.7×10^6	2-3	3.4×10^4
17.	Toluene-2,4-diamine	--	--	--	--	Probable	4.4×10^5	--	5.3×10^3

(continued)

TABLE 2 (continued)

	Solubility parameter [4,5]				Pollutant information [2]			
	δ Calc[a] [4]	Calc Sm[b]	Lit Sm[b]	δ Lit[a] [5]	Carcinogen	Emissions, kg[c]	Half life, da	Priority,[d] kg
18. Vinyl acetate	8.9	769	--	--	Possible	6.8×10^5	--	2.2×10^3
19. Ethylene dibromide	10.9	2053	--	--	Probable	2.1×10^6	<0.83	2.0×10^4
20. 1,3-Dichloropropene	11.9	1318	--	--	Possible	2.2×10^7	3	7.3×10^4
	11.6	1314	--	--				

[a] $(2.045\ J^{1/2})/cm^3$.

[b] $(2.045\ g\ J^{1/2})/(cm^3 \cdot mol)$.

[c] Emissions, kg = source emissions, kg/yr (365 da) x half life, 1 da.

[d] Priority, kg = emissions, kg x average mutagenic potency relative to benzo(a)pyrene.

KEY

CAS No. - Chemical Abstract Service Number
M.W. - Molecular Weight
Den. - Density
M.P. - Melting Point
B.P. - Boiling Point

Vap. P. - Vapor Pressure
calc - Calculated
lit - Literature
subl - Sublimes
decom - Decomposes

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[5] Burrell, H., and B. Immergut. Solubility Parameter Values. In: Polymer Handbook, J. Brandup and E. H. Immergut, Eds. Interscience Publishers, New York, New York, 1966. pp. IV-341 - IV-368.

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TABLE 3. HAZARDOUS PROPERTIES OF SELECTED COMPOUNDS

		Sax hazard information [7]														
							Disaster			Health hazard ratings						
				Fire						Acute local				Acute syst		
	Compound	Flash point, °C(°F)	TLV, ppm	Heat	Flame	Expl	Rx wi oxid	Toxic fume	Expl (Rx)	Irr	All	Ing	Inh	Ing	Inh	SAb
1.	Acrolein	<-18 (<0)	0.01	V Dang	V Dang	V Dang	V Dang			3	1	3	3	3	3	2
2.	Acrylonitrile	-1 (30)	20	Dang	Dang		Dang							Highly toxic		
3.	Benzene	-11 (12)		Dang	Dang		Dang			2		1	1	2	2	2
4.	Benzidine							Dang		U	U	U	U	3	3	3
5.	Benzo(a)pyrene															
6.	Benzyl chloride	67 (153)	1	Mod	Mod		Dang		Mod	3		3	3	3	3	3
7.	Carbon tetra-chloride	none	10					Dang		0	0	0	0	3	3	1
8.	Chrysene															
	Cumene hydro-peroxide	79 (175)		Mod	Mod				Dang	3		3	3	3	3	3
9.	Di-(2-ethylhexyl) phthalate (DEHP)	218 (425)		Slt	Slt					0	0	1	1			
10.	1,4-Dioxane	12 (54)	9	Dang	Dang		Dang			2				3	3	3
11.	Ethylene dichloride	13 (56)	50	Dang	Dang		Dang	?		3				3	3	
12.	Ethylene oxide	<-18 (<0)	50	SVR	SVR	SVR	SVR		SVR	3					2	
13.	Hexachloro-1,3-butadiene							?								
14.	Pentachlorophenol							Dang		3				3	3	2
15.	Styrene	31 (88)	100	Dang	Mod		Dang			2				2	2	
16.	Tetrachloroethylene	none	100					Dang		2				3	2	2
	Tetraethyl lead			Mod	Mod		Dang							Highly toxic		
17.	Toluene-2,4-diamine							Mod		2				2	2	
18.	Vinyl acetate	-8 (18)	10	V Dang	V Dang		V Dang			1				1		
19.	Ethylene dibromide	none	20						Dang	3				3	3	3
20.	1,3-Dichloro-propene	35 (95)		Mod	Mod		Dang	?		2		2	2	2	-	-

(continued)

TABLE 3 (continued)

Compound	Sax hazard information [7]					Patty hazard information [8]				General description
	Health hazard ratings									
	Chr loc		Chro syst							
	Irr	All	Ing	Inh	SAb	Flash point, °C(°F)	Auto ig temperature, °C(°F)	TLV, ppm	Oral LD_{50}, mg/kg	
1. Acrolein	3	1	U	U	U	<-18 (<0)			66	Irritant, highly toxic; flammable.
2. Acrylonitrile			Highly toxic			-3 (27)	482 (900)	20	35-90	Irritant, highly toxic; flammable.
3. Benzene	0	0	3	3	3	-11 (12)		25		Toxic, flammable.
4. Benzidine	U	U	3	3	3					Extremely toxic and carcinogenic.
5. Benzo(a)pyrene										Toxic and carcinogenic.
6. Benzyl chloride	U	U	U	U	U					Irritant, rxts with oxidizers, toxic.
7. Carbon tetrachloride	1		3	3	3	none	none	10	2,920	Toxic.
8. Chrysene										Toxic and carcinogenic.
Cumene hydroperoxide	U	U	U	U	U					Irritant, toxic, oxidizer rxts violently.
9. Di-(2-ethylhexyl) phthalate (DEHP)	0	0	2	2	1	218 (425)			24,000 35,000	Low toxicity-plasticizer.
10. 1,4-Dioxane	U	U	3	3	2	18 (65)		100	3,000 6,000	Toxic, irritant; flammable.
11. Ethylene dichloride	2		3	3	2	18 (65)	413 (775)	100	680	Very toxic irritant; flammable.
12. Ethylene oxide	2				U	-20 (-4)		50	100-100	Very toxic, irritant, highly flammable; rxts with oxidizers; explosion hazard.
13. Hexachloro-1,3-butadiene										Toxic and carcinogenic.
14. Pentachlorophenol			2	2	2			0.046	20-200	Highly toxic, irritant.
15. Styrene	U	U	2	2	-	30 (86)		100		Irritant, toxic; mod, flammable.
16. Tetrachloroethylene	2		2	2	2	none		100		Anesthetic; toxic.
Tetraethyl lead			Extremely toxic							Extremely toxic.
17. Toluene-2,4-diamine	U	U	2	2						Toxic.
18. Vinyl acetate	1		U	U	U	-22 (8)			2,900	Flammable; toxic.
19. Ethylene dibromide	2		2	2	2	none		25	60-500	Highly toxic; irritant.
20. 1,3-Dichloropropene	U	U	U	U	U					Irritant; flammable; toxic.

HEALTH HAZARD RATINGS

0 - None
1 - Slight
2 - Moderate
3 - High
U - Unknown

KEY

Acute syst - Acute systemic
All - Allergen
Auto ig - Autoignition
Chr loc - Chronic local
Chr syst - Chronic systemic
Dang - Dangerous
Expl - Explosion
Expl (Rx) - Explosion by reaction
Ing - Ingestion
Inh - Inhalation
Irr - Irritant
Mod - Moderate
Rx wi oxid - Reacts with oxides
SAb - Skin Absorption
Slt - Slight
SVR - Severe
Temp - Temperature
V Dang - Very Dangerous

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[7] Sax, N. I. Dangerous Properties of Industrial Chemicals. Van Nostrand Reinhold Company, Cincinnati, Ohio, 1975.

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TABLE 4. MASS SPECTRAL INFORMATION FOR SELECTED COMPOUNDS [9]

Compound	Molecular weight, g/mol	Emperical formula	Eight major MS peaks [m/z ratio (relative intensity)] 1	2	3	4	5	6	7	8
Acrolein	56	C_3H_4O	27 (100)	56 (83)	25 (70)	55 (64)	28 (51)	26 (49)	29 (43)	18 (31)
			27 (100)	56 (65)	26 (59)	28 (53)	55 (44)	29 (39)	25 (9)	14 (4)
			27 (100)	56 (70)	28 (60)	26 (53)	55 (49)	29 (40)	25 (8)	53 (5)
			27 (100)	56 (74)	28 (66)	26 (54)	55 (53)	29 (37)	25 (8)	38 (5)
			27 (100)	26 (57)	56 (55)	28 (48)	29 (44)	55 (39)	31 (8)	37 (7)
Acrylonitrile	53	C_3H_3N	26 (100)	53 (99)	52 (75)	51 (32)	27 (18)	25 (10)	50 (8)	38 (7)
			26 (100)	53 (92)	52 (75)	51 (33)	27 (23)	25 (11)	38 (10)	50 (8)
			53 (100)	52 (73)	26 (70)	51 (28)	28 (10)	27 (9)	50 (7)	25 (4)
			53 (100)	26 (93)	52 (79)	51 (30)	27 (12)	50 (7)	25 (5)	54 (5)
			26 (100)	53 (96)	52 (73)	51 (32)	27 (22)	28 (13)	25 (12)	38 (9)
			53 (100)	26 (70)	52 (69)	51 (27)	27 (10)	50 (7)	25 (4)	54 (3)
			53 (100)	26 (97)	52 (75)	28 (41)	51 (36)	27 (23)	25 (10)	50 (10)
Benzene	78	C_6H_6	78 (100)	77 (19)	51 (19)	52 (17)	50 (14)	39 (12)	79 (9)	76 (6)
			78 (100)	52 (19)	51 (18)	50 (16)	77 (14)	39 (13)	79 (6)	76 (6)
			78 (100)	52 (18)	77 (17)	51 (16)	50 (13)	39 (10)	79 (5)	74 (5)
			78 (100)	51 (21)	52 (20)	50 (18)	39 (14)	77 (14)	79 (7)	38 (6)
			78 (100)	52 (18)	51 (17)	77 (15)	50 (14)	39 (11)	79 (7)	76 (5)
			78 (100)	52 (19)	77 (18)	51 (16)	39 (13)	50 (13)	79 (7)	76 (6)
			78 (100)	77 (19)	52 (15)	51 (13)	50 (10)	39 (9)	79 (6)	74 (4)
			78 (100)	77 (24)	52 (18)	51 (15)	39 (12)	50 (12)	79 (7)	75 (5)
			78 (100)	77 (19)	52 (15)	51 (13)	39 (10)	50 (9)	79 (7)	76 (5)
			78 (100)	77 (19)	52 (16)	51 (15)	50 (11)	39 (10)	79 (6)	76 (5)
			78 (100)	52 (25)	77 (23)	51 (16)	50 (15)	79 (10)	74 (5)	76 (4)
Benzidine	184	$C_{12}H_{12}H_2$	184 (100)	92 (15)	183 (12)	185 (12)	156 (6)	167 (5)	182 (4)	166 (4)
			184 (100)	185 (15)	183 (11)	92 (8)	36 (7)	156 (4)	182 (4)	167 (4)
Benzo(a)pyrene	252	$C_{20}H_{12}$	252 (100)	126 (23)	253 (21)	250 (16)	125 (15)	113 (9)	112 (7)	126 (7)
Benzyl chloride	126	C_7H_7Cl	91 (100)	126 (28)	128 (9)	65 (9)	92 (8)	63 (6)	39 (5)	89 (5)
			91 (100)	126 (23)	2 (15)	19 (13)	65 (12)	63 (10)	92 (9)	128 (7)
			91 (100)	126 (22)	92 (16)	63 (12)	39 (6)	128 (5)	28 (5)	45 (5)
			91 (100)	126 (28)	65 (9)	92 (8)	63 (6)	89 (5)	39 (5)	125 (4)
Carbon tetrachloride	152	CCl_4	117 (100)	119 (99)	121 (34)	82 (22)	46 (20)	84 (15)	35 (14)	36 (12)
			117 (100)	119 (96)	121 (32)	82 (24)	47 (21)	84 (15)	35 (11)	49 (7)
			117 (100)	119 (97)	121 (32)	82 (19)	47 (13)	84 (13)	35 (6)	49 (4)
			117 (100)	119 (96)	47 (48)	35 (44)	82 (30)	121 (30)	84 (19)	49 (15)
Chrysene	228	$C_{18}H_{12}$	228 (100)	226 (20)	229 (19)	114 (15)	113 (13)	44 (10)	101 (7)	227 (6)
			228 (100)	226 (25)	229 (20)	113 (18)	114 (17)	101 (10)	227 (9)	100 (8)
			228 (100)	226 (22)	229 (19)	114 (16)	113 (14)	101 (9)	227 (7)	100 (6)
Cumene hydroperoxide	152	$C_9H_{12}O_2$	43 (100)	119 (91)	105 (76)	121 (74)	77 (67)	91 (43)	120 (33)	51 (30)
			43 (100)	105 (77)	121 (41)	77 (42)	51 (26)	120 (19)	78 (13)	39 (11)

(continued)

TABLE 4 (continued)

Compound	Molecular weight, g/mol	Empirical formula	Eight major MS peaks [m/e ratio (relative intensity)]							
			1	2	3	4	5	6	7	8
Di-(2-ethylhexyl) phthalate	390	$C_{24}H_{38}O_4$	149 (100)	57 (72)	43 (48)	41 (42)	54 (39)	167 (38)	70 (30)	55 (28)
			149 (100)	279 (51)	167 (39)	57 (32)	70 (26)	71 (21)	55 (19)	121 (17)
			149 (100)	279 (64)	167 (46)	57 (16)	113 (14)	114 (14)	156 (14)	280 (14)
			149 (100)	57 (73)	43 (50)	41 (50)	105 (44)	167 (42)	74 (37)	56 (17)
			149 (100)	57 (37)	167 (27)	43 (27)	70 (23)	71 (23)	41 (22)	55 (17)
			149 (100)	57 (54)	169 (13)	71 (27)	70 (27)	43 (20)	55 (19)	113 (14)
			57 (100)	44 (99)	55 (79)	41 (65)	70 (60)	43 (46)	72 (45)	56 (28)
			149 (100)	57 (48)	43 (28)	71 (24)	41 (20)	55 (18)	279 (17)	167 (16)
1,4-Dioxane	88	$C_4H_8O_2$	28 (100)	29 (37)	88 (31)	58 (24)	15 (17)	31 (17)	27 (15)	30 (13)
			28 (100)	88 (53)	58 (40)	29 (28)	31 (16)	30 (15)	43 (12)	15 (11)
			28 (100)	88 (36)	58 (32)	29 (27)	31 (16)	30 (14)	15 (11)	43 (10)
			28 (100)	88 (54)	58 (44)	29 (32)	43 (17)	27 (11)	57 (11)	30 (11)
			28 (100)	58 (68)	29 (54)	31 (31)	43 (27)	27 (24)	30 (24)	57 (19)
			28 (100)	29 (32)	58 (24)	88 (22)	31 (16)	27 (15)	30 (13)	41 (11)
Ethylene dichloride	98	$C_2H_4Cl_2$	62 (100)	27 (70)	49 (50)	64 (33)	63 (27)	98 (23)	51 (17)	61 (16)
			62 (100)	27 (86)	49 (37)	64 (32)	26 (29)	63 (17)	51 (11)	61 (11)
			62 (100)	27 (91)	49 (40)	64 (32)	26 (31)	63 (19)	98 (14)	51 (13)
Ethylene oxide	44	C_2H_4O	29 (100)	44 (79)	15 (55)	43 (23)	14 (21)	42 (17)	28 (9)	16 (8)
			44 (100)	29 (98)	15 (50)	43 (23)	42 (15)	14 (13)	16 (6)	28 (4)
			29 (100)	15 (65)	44 (65)	14 (26)	43 (16)	26 (14)	42 (12)	13 (8)
			44 (100)	29 (83)	15 (53)	43 (22)	42 (13)	14 (12)	16 (3)	45 (3)
Hexachloro-1,3-butadiene	258	C_4Cl_6	225 (100)	227 (65)	223 (63)	190 (43)	260 (36)	188 (32)	118 (30)	141 (29)
			225 (100)	227 (64)	223 (63)	260 (43)	190 (39)	262 (34)	188 (30)	141 (26)
Pentachlorophenol	264	C_6HOCl_5	266 (100)	268 (70)	264 (68)	165 (54)	167 (52)	95 (44)	130 (30)	60 (28)
			266 (100)	268 (65)	264 (63)	165 (29)	36 (29)	167 (28)	270 (23)	230 (18)
Styrene	104	C_8H_8	104 (100)	103 (38)	78 (31)	51 (30)	77 (20)	50 (15)	39 (11)	52 (11)
			104 (100)	102 (69)	51 (45)	103 (39)	78 (24)	39 (23)	50 (19)	52 (16)
			104 (100)	103 (45)	78 (32)	51 (21)	77 (17)	105 (9)	50 (7)	52 (7)
			104 (100)	103 (38)	78 (27)	51 (25)	77 (17)	50 (9)	52 (9)	105 (9)
Tetrachloro-ethylene	164	C_2Cl_4	166 (100)	164 (78)	129 (64)	131 (62)	168 (48)	94 (21)	133 (20)	96 (14)
			166 (100)	164 (79)	129 (69)	131 (66)	168 (48)	47 (42)	94 (40)	35 (35)
			166 (100)	164 (79)	129 (61)	131 (58)	168 (46)	94 (28)	133 (19)	96 (18)
Toluene-2,4-diamine	122	$C_7H_{10}N_2$	121 (100)	122 (15)	94 (10)	105 (8)	104 (8)	77 (5)	61 (5)	123 (4)
Vinyl acetate	86	$C_4H_6O_2$	43 (100)	15 (15)	28 (10)	27 (8)	42 (8)	86 (5)	44 (5)	14 (4)
			43 (100)	15 (9)	86 (9)	27 (6)	42 (5)	44 (4)	28 (4)	29 (2)
			43 (100)	45 (26)	28 (25)	60 (14)	29 (14)	42 (13)	44 (13)	27 (6)
			43 (100)	15 (13)	86 (6)	27 (6)	42 (5)	44 (5)	28 (3)	14 (3)
Ethylene dibromide	186	$C_2H_4Br_2$	107 (100)	109 (95)	27 (54)	28 (11)	26 (8)	93 (5)	188 (5)	95 (4)
			27 (100)	107 (77)	109 (72)	26 (24)	28 (10)	79 (5)	25 (5)	93 (4)
1,3-Dichloropropene	110	$C_3H_4Cl_2$	75 (100)	39 (55)	77 (32)	49 (26)	110 (20)	38 (14)	112 (13)	36 (10)
			75 (100)	77 (33)	39 (33)	110 (25)	49 (17)	112 (16)	38 (6)	51 (6)

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[9] Eight Peak Index of Mass Spectra, 2nd ed., Vol. I. Mass Spectrometry Data Centre, Aldermaston, Reading, U.K., 1974.

TABLE 5. DIRECTORY OF INFORMATION CONTAINED IN LITERATURE REFERENCES

	References																		
Information	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28
Compounds																			
Acrolein			P[a]	all pertain															
Acrylonitrile		P	P											x				x	
Benzene		x	x		x	x	P				x			x				x	
Benzidine			P					P?											
Benzo(a)pyrene	x							x					x				x		
Benzyl chloride		x	P		P							x							
Carbon tetrachloride		P	x		x	P	P							x					
Chrysene	P							x					P				x		
Cumene hydroperoxide																			
Di-(2-ethylhexyl)phthalate			x					x							x	x		P	
Dioxane		x	P							x									
Ethylene dichloride		P	P		P	P	P							x					
Ethylene oxide		x	x			x			x					x					
Hexachloro-1,3-butadiene			P					P							P?	P?			
Pentachlorophenol		P	P					x							P?	P?			
Styrene		P	x		P	x	x					P						x	
Tetrachloroethylene		P	x		x	x	P							x					
Tetraethyl lead																			x
Toluene-2,4-diamine																			
Vinyl acetate		P	P				P												
Ethylene dibromide		P	P		P	P	P							x					
1,3-Dichloropropene		P	P		P	P	P							x					
Sampling:																			
Type of Sample																			
Ambient Air	x	x	x			x		x					x		x	x	x		x
Workplace Air	x	x	x				x		x	x	x	x			x			x	
Other Air	x		x										x	x					
Water (only)					x														
Method of Sampling																			
Solid Sorbent			x		x	x	x	x		x	x	x			x	x		x	x
Type[b]			var[c]		Tx	Tx	AC	Tx		AC	AC	Tx			Fal	Fal		Fal, SG, AC	var
Other[d]	F	B	var					F	I				F				F		F
Particulate Assoc.	x							x					x				x		x
Analysis:																			
Desorption (S,T)[e]	S		S&T		T	T	S	S		S	S	T	S		S	S	S	S	
Solvent[f]	cyh		var				CS_2	Bz, MeOH		CS_2	CS_2		cyh		pet eth, et eth	pet eth, et eth		MeOH, CS_2, et ace	
Temp (°C)																			
Resolution[g]	GC		var		CGC	CGC	GC	GC	GC	GC	GC	GC	HPLC		GC	GC		GC	var
Detection[h]	Fl	IR	var		MS	MS	FID	MS		FID	FID	MS	Fl&UV		EC	EC		FID &MS	var
Results																			
Quantitative	x		x		x	x	x	x	x	x		x	x		x	x		x	x
Qualitative		x						x											x
General Information:				x							x			x			x		x
Safety				x															
Previous Lit.											x								x
Mutagenicity														x					
Sampling Data																	x		
Basic Research																			

	References																	
Information	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46
Compounds																		
Acrolein	all pertain	x												all pertain				x
Acrylonitrile			x					x										
Benzene								x			x							
Benzidine																		
Benzo(a)pyrene						x	x		x	P					x			
Benzyl chloride																		
Carbon tetrachloride								x	P		x		x			x		
Chrysene						P	P		x	P					P			
Cumene hydroperoxide																		
Di-(2-ethylhexyl)phthalate																		
Dioxane											x							
Ethylene dichloride								x	P		x		P			x		
Ethylene oxide																		
Hexachloro-1,3-butadiene				x														
Pentachlorophenol																	P	
Styrene					x													
Tetrachloroethylene								x	P		P		x			x		
Tetraethyl lead												x						
Toluene-2,4-diamine																		
Vinyl acetate								x										P
Ethylene dibromide								x	P		P		P			P		
1,3-Dichloropropene								x	P		P		P			P		
Sampling:																		
Type of Sample																		
Ambient Air				x		x	x			x		x	x	x	x			
Workplace Air	x	x	x	x	x			x	x		x			x		x	x	
Other Air				x										x				x
Water (only)																		
Method of Sampling																		
Solid Sorbent	x	x		x	x			x	x		x		x	x		x	x	x
Type[b]	var	AC		Tx	AC			AC	AC		AC		PoN	var		AC	AC	Tx
Other[d]	F		D	F		F	F		F	F					F			
Particulate Assoc.	x			x		x	x		x	x		x			x			
Analysis:																		
Desorption (S,T)[e]	S	S		S	S	S	S		S	S	S		T	S&T	S	S	S	T
Solvent[f]	var	et DiCl		hex	CS_2	Bz	Cyh		CS_2 Cyh	Bz	CS_2				?	CS_2	et eth	
Temp (°C)													200					250
Resolution[g]	GC	GC		GC	GC	TLC	GC		GC& CC	CC& TLC	GC		GC		TLC	GC	GC	GC
Detection[h]	AA& FID	FID	IR	EC	FID	Fl	Fl	FID	FID &UV	UV-Vis &Fl	FID		EC& MS		Fl	MS	FID	FID
Results																		
Quantitative		x	x	x	x		x		x	x	x		x	x	x	x	x	x
Qualitative			x			x												
General Information:	x							x		x	x	x		x		x		
Safety	x																	
Previous Lit.												x						
Mutagenicity																		
Sampling Data										x	x							
Basic Research								x			x			x		x		

[a] P - this article pertains to this compound since similar compounds are utilized.

[b] Type of Sorbent
AC - Activated charcoal
Fal - Florisil
PoN - Porapak N
SG - Silica Gel
Tx - Tenax GC

[c] var - various

[d] Other sampling methods
B - Bag (usu. Tedlar)
D - Direct sample
I - Impinger
F - Filter

[e] S - solvent; T - thermal

[f] Solvents
Bz - benzene
CS_2 - carbon disulfide
chy - cyclohexane
et ace - ethyl acetate
et DiCl - ethylene dichloride
et eth - ethyl ether
hex - hexane
MeOH - methanol
pet eth - petroleum ether

[g] Resolution technique
CC - Column chromatography
CGC - Capillary gas chrom
GC - Gas chromatography
HPLC - High performance
TLC - Thin layer chrom.

[h] Detection technique
AA - Atomic adsorption
EC - Electron capture
Fl - Fluorescence
FID - Flame ionization det.
IR - Infrared spec.
MS - Mass spec.
UV - Ultra-violet spec.
Vis - Visible spec.

See references on the following pages.

TABLE 5 (continued)

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TABLE 6. CONCENTRATIONS OF VARIOUS COMPOUNDS IN AIR SAMPLES REPORTED IN LITERATURE REFERENCES

Compound	Concentration	Reference	Type of air sample
Benzene	1.3-15 ppb[a]	12	Ambient
	1.3-15 ppb	15	Ambient
Benzo(a)pyrene	[with B(e)P & perylene]		
	8 - 40 ng/m^3	17	Ambient
	1 - 3 ng/m^3	22	Ambient
	200 - 300 ng/m^3	22	Downwind from coke oven
	0.1 - 2.0 ng/m^3	26	Los Angeles, CA
	0.122 - 1.76 ng/m^3	35	Urban areas
	ND - 57 ng/m^3	37	Rubber factory (outside)
	0.003 - 1.98 ng/m^3	43	Charleston, SC
Carbon tetrachloride	30 - 130 ppt	41	Ambient
Chrysene	[with B(a)A]		
	5 - 30 ng/m^3	17	Ambient
	0.2 - 2.0 ng/m^3	26	Los Angeles, CA
DDT	0.002 - 0.09 ng/m^3	25	Over open ocean
Dibutyl phthalate	0.08 - 2.5 ng/m^3	25	Over open ocean
Di-(2-ethylhexyl) phthalate	(phthalate ester)		
	>10 mg/m^3	12	Car interior
	126 - 200 ng/m^3	17	Ambient
	30 - 70 ng/m^3	24	Office area
	0.4 - 3,370 ng/m^3	28	Ambient (various)
Pentachlorophenol	1 - 3 ng/m^3	17	Ambient
Perchloroethylene (tetrachloroethylene)	30 - 130 ppt	41	Ambient
Polychlorinated biphenyls (PCB)	35 - 90 ng/m^3	24	Office area
	0.1 - 1.0 ng/m^3	25	Over open ocean

[a] Information in both references provided by the same authors.

in their adsorption characteristics, such that the compounds of interest could be collected using a single portable sampling system.

The analytical technique determined to be most suitable for the determination of the twenty compounds was gas chromatography combined with mass spectroscopy (GC/MS). Gas chromatography has been used in various applications for all twenty of the compounds of interest. Mass spectroscopy is also widely applicable and aids in compound identification/confirmation by producing mass spectra for compounds eluting from a chromatograph. To further aid in compound identification by retention time data, maximum gas chromatographic resolution, through the use of capillary columns, was desired.

The technique of compound desorption, thermal or solvent, from the sorbent materials prior to GC/MS analysis was to be determined experimentally. The greater sensitivity attainable by thermal desorption was to be evaluated in comparison to the greater compound stability and (frequently, though not necessarily) more reproducible desorption efficiencies attainable by solvent desorption.

The literature survey of the twenty, selected, target compounds indicated significant difficulties associated with the sampling of two compounds originally selected for this study: tetraethyl lead and cumene hydroperoxide. Tetraethyl lead was found to be an extremely toxic compound which to obtain required an on-site inspection of laboratory facilities by its supplier. In addition, it was indicated to be a relatively unstable compound that readily thermally degrades and that may not persist in the atmosphere [20, 32] as a pollutant. Cumene hydroperoxide was found to be a very strong oxidizing agent which also would not likely persist in the atmosphere due to its extreme reactivity. Such a reactive compound was thought to present a particular problem with potential *in-situ* reactions when concentrated in a sorbent cartridge. Therefore, these two compounds, tetraethyl lead and cumene hydroperoxide, were replaced as compounds of interest by two alternate compounds, ethylene dibromide and 1,3-dichloropropene (cis and trans isomers).

A few general problems were found to be associated with the twenty selected compounds. For example, highly volatile compounds could not be quantitatively retained on solid sorbents if the sampling volume was very high; while non-volatile compounds, such as benzo(a)pyrene, which exist in the atmosphere at concentrations lower than volatile compounds, generally could not be detected analytically without very high sampling volumes. Another problem was that reactive compounds, such as styrene and ethylene oxide, which tend to polymerize on active surfaces, were more effectively retained on sorbents which had relatively more active surfaces. These paradoxes indicated areas where compromises would be required to obtain a single sampling system.

SECTION 6

DEVELOPMENT OF THE ANALYTICAL METHOD

OBJECTIVE

The analytical technique determined to be most suitable for the determination of the twenty selected compounds was capillary gas chromatography [$(GC)^2$] combined with mass spectroscopy (MS). In order to be cost and time effective, it was decided that the capillary gas chromatographic technique should be developed prior to interfacing with a mass spectrometer. Ideally, this $(GC)^2$ technique was to allow the separation of the compounds of interest, to be adaptable to mass spectrometric detection, and to permit the introduction of sorbent tube samples obtained by either solvent or thermal desorption. This analytical technique was to be used for the laboratory development and evaluation of the multi-residue, portable miniature collection system, as well as for the analyses of field samples (after MS interfacing).

INSTRUMENTATION

A Hewlett-Packard Model 5840 gas chromatograph (GC) was dedicated to this contract during the development of the analytical method. This instrument had dual flame ionization detectors (FID) and a printer/plotter terminal with microprocessing and integration capabilities. In addition, the instrument could be used with capillary GC columns, in either a split or splitless injection mode, and with packed GC columns. A liquid nitrogen cryogenic option was installed in the instrument during the course of the analytical method development work. This instrument was selected as being particularly suitable to this contract because a Hewlett-Packard Model 5985 GC/MS instrument was to be used for later analyses. The chromatograph on the GC/MS instrument is also a Hewlett-Packard Model 5840 GC, almost identical to the instrument selected for developing the analytical method.

EVALUATIONS

Columns

Several GC capillary columns were evaluated for their suitability for the analysis of the twenty compounds selected for this program. Five columns were evaluated during the analytical method development work performed on the Hewlett-Packard Model 5840 GC; a few other columns were tried later during GC/MS interfacing and field sample analyses. The five columns investigated with the Hewlett-Packard Model 5840 GC included:

- An ~48 m long, ~0.25 mm ID, Carbowax 20 M wall-coated, open-tubular (WCOT) glass column.
- An ~50 m long, ~0.50 mm ID, Carbowax 20 M wall-coated, open-tubular, glass column.
- An ~50 m long, ~0.20 mm ID, Carbowax 20 M wall-coated, open-tubular, fused-silica column.
- An ~50 m long, ~0.20 mm ID, OV-101 wall-coated, open-tubular, fused-silica column.
- An ~45 m long, ~0.50 mm ID, SP2100 support-coated, open-tubular (SCOT), glass column.

These columns were coated with three types of liquid phases, Carbowax 20 M, OV-101, and SP2100. Carbowax 20 M is a polar phase, and OV-101 and SP2100 are non-polar methyl-silicone phases that are approximately equivalent. Different types of capillary columns also are represented by these five columns including a wide-bore SCOT glass column, a wide-bore WCOT glass column, a regular-bore WCOT glass column and two narrow-bore fused silica columns.

These columns were assessed for their ability to chromatograph the twenty compounds of interest by installing them within the GC using direct injection port and detector connections. The headspace samples or standard analytical mixtures of these compounds were injected into the GC. The results of these experiments are compiled in Table 7. Although chromatographic conditions were varied with the evaluation of each column, Table 7 still demonstrates the comparative abilities of the columns to chromatograph and separate the compounds of interest.

The retention times indicate the columns' abilities to separate these compounds. Compounds with retention time differences of less than ~0.15 min usually co-eluted during the analysis of a mixture. For example, tetrachloroethylene (RT = 5.25 min) and acrylonitrile (RT = 5.27 min) were found to co-elute when analyzed together on an ~0.25 mm ID, Carbowax 20 M WCOT column (column A in Table 7). All columns were found to have at least two co-eluting compounds, although which compounds co-eluted varied from column to column. To help separate compounds as best as they could be separated, all columns but one were evaluated using close to optimal conditions. These conditions included very slow temperature programming (2 or 3°C/min) from a low temperature (0° or 35°C) to an upper temperature ~30°C below the columns' temperature limits. The exception was the wide-bore

TABLE 7. CHROMATOGRAPHIC PROPERTIES OF THE TWENTY SELECTED COMPOUNDS ON VARIOUS CAPILLARY COLUMNS

Compound	Column A		Column B		Column C		Column D		Column E	
	R.T., min	Peak shape	R.T., min	Peak shape	R.T., min	Peak shape	R.T., min	Peak shape	R.T., min	Peak shape
Propane[a]	2.84	1	NE	NE	NE	NE	NE	NE	3.09	1
Ethylene oxide	NE	NE	NE	NE	NE	NE	NE	NE	6.79	5
Acrolein	3.46	3	NE	NE	3.71	2	NE	NE	4.17	5
Carbon tetrachloride	3.63	2	NE	NE	3.88	1	NE	NE	8.22	3
Vinyl acetate	3.76	2	NE	NE	4.00	2	6.33	2	5.75	4
Benzene	4.06	1	NE	NE	4.39	2	9.10	1	8.11	2
Tetrachloroethylene	5.25	1	NE	NE	5.54	1	18.94	2	19.38	3
Acrylonitrile	5.27	3	NE	NE	5.12	2	5.54	2	8.38	5
Ethylene dichloride	5.99	2	NE	NE	6.72	1	8.51	2	7.35	3
1,4-Dioxane	6.25	2	NE	NE	6.41	2	11.51	2	4.22	2
Ethylene dibromide	14.77	2	NE	NE	NE	NE	17.97	2	17.71	3
cis-1,3-Dichloropropene	15.24	2	NE	NE	NE	NE	15.70	2	∿13	3
trans-1,3-Dichloropropene	9.26	2	NE	NE	NE	NE	13.70	2	NE	NE
Styrene	17.23	3	NE	NE	UN	2	25.82	2	23.74	3
Benzyl chloride	34.76	3	2.78	2	UN	2	36.48	2	27.87	2
Ethylene glycol[b]	39.44	4	3.72	2	UN	3	86.45	2	20.10	5
Hexachloro-1,3-butadiene	40.22	2	2.69	2	UN	2	53.49	2	31.79	3
Toluene-2,4-diamine	84.83	3	NE	NE	NE	NE	68.67	2	34.71	5
Di-(2-ethylhexyl)phthalate	133.01	2	>95	3	UN	2	151.73	3	∿26	5
Pentachlorophenol	ND	ND	ND	ND	ND	ND	ND	ND	38.56	3
Benzidine	ND	ND	NE	NE	ND	ND	111.21	2	48.33	5
Chrysene	ND	ND	NE	NE	ND	ND	131.15	3	64.66	3
Benzo(a)pyrene	ND	ND	NE	NE	ND	ND	213.03	4	∿107	4

[a] Propane was used to determine column dead volume.

[b] Ethylene glycol is a polymerization product of ethylene oxide.

KEY

NE - Not evaluated
ND - Not detected
UN - Unknown
RT - Retention time

Peak Shape:

1 - Excellent
2 - Good
3 - Fair
4 - Poor
5 - Very poor

Columns:

A - Carbowax 20 M wall-coated, open-tubular, glass column, ∿0.25 mm ID, ∿48 m long
B - Carbowax 20 M wall-coated, open-tubular, glass column, ∿0.50 mm ID, ∿50 m long
C - Carbowax 20 M wall-coated, open-tubular, fused-silica column, ∿0.20 mm ID, ∿50 m long
D - OV-101 wall-coated, open-tubular, fused-silica column, ∿0.2 mm ID, ∿50 m long
E - SP2100 support-coated, open-tubular, glass column, 0.50 mm ID, ∿45 m long

(~0.50 mm ID) Carbowax 20 M WCOT column (column B in Table 7). Column B was evaluated isothermally near its upper temperature limit to determine whether high-boiling compounds such as di-(2-ethylhexyl) phthalate and pentachlorophenol would elute significantly faster (in less than ~60 min) than from a similar narrow-bore column (column A). Unfortunately, these high-boiling compounds did not quickly elute from the wide-bore column (column B) either. Indeed, all compounds in Table 7 indicated as "not detected" did not appear to elute during the analysis time allotted (100 to 220 min). High boiling compounds did not appear to elute from any of the Carbowax 20 M coated capillary columns under the analytical conditions evaluated.

How a column interacts with a compound eluting through it is demonstrated by the peak shape of the resulting chromatogram. A very sharp, well-shaped peak indicates "good" chromatographic interaction, whereas a tailing, broad, or skewed peak indicates "poor" chromatographic interaction. The chromatographic interactions of the twenty selected compounds with the various capillary columns were evaluated by rating the peak shapes of their chromatograms as indicated in Table 7. Generally, tailing was the major problem observed and ranged from slight to very extreme. A peak shape rating of at least a 3 (Fair), preferably a 2 (Good), was considered adequate for permitting compound quantitation. The SCOT column (Column E) demonstrated the poorest chromatographic ability with badly tailing peaks observed for polar compounds such as ethylene oxide, acrylonitrile, and ethylene glycol. All of the other columns exhibited reasonable chromatograms for most of the compounds with the fused-silica columns giving especially good results.

As a result of these analyses, ethylene oxide was eliminated from the list of compounds to be investigated because it so readily reacted to form ethylene glycol and other products. Instead, both of the isomers of 1,3-dichloropropene were to be evaluated. Ethylene glycol was included in most of the subsequent analyses as a compound which might be of interest later. Although ethylene glycol doesn't exhibit carcinogenic potential [2], its presence in a sample could indicate the possible presence of ethylene oxide.

Column test mixtures, as suggested in the literature [47], were prepared to further evaluate the performance of the capillary columns. These mixtures are given in Tables 8 and 9 and typical chromatograms are shown in Figures 2 and 3. They were useful in evaluating a number of chromatographic phenomena arising from column and system characteristics. Specifically, the normal

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[47] Cram, S. P., F. J. Yang, A. C. Brown III. Characterization of High Performance Glass Capillary Gas Chromatography. Chromatographia, 10(8), 1977.

TABLE 8. COMPOSITION OF COLUMN TEXT MIXTURE IIb

Compound	M.W., g/mol	Density, g/mL	Amount in 10 mL MeOH, mg	Conc., ppm (wt/wt)	Amount in 1 mL inj., µg	Amount to $(GC)^2$ Det.,[a] ng
C_{12}	170.33	0.751	28.9	3,910	3.10	15.5
C_{13}	184.36	0.757	13.3	3,645	2.89	14.5
DMA	121.18	0.974	18.7	2,359	1.87	9.4
DMP	122.16	1.036	15.7	1,980	1.57	7.9
2-Ethyl hexanol	130.23	0.834	31.6	3,986	3.16	15.8
Naphthalene	128.16	1.145	31.0	3,910	3.10	15.5
2-Octanone	128.21	0.818	18.0	2,270	1.80	9.00
MeOH[b]	32.04	0.793	-	-	-	-

[a] Assuming a 200 to 1 split ratio.

[b] Solvent.

TABLE 9. COMPOSITION OF COLUMN TEST MIXTURE IIIa

Compound	Concentration, µg/mL	Amount in 1 µL injection, ng	Amount to detector,[a] ng
$n\text{-}C_{10}$	312	312	3.12
$n\text{-}C_{13}$	346	346	3.46
$n\text{-}C_{16}$	356	356	3.56
$n\text{-}C_{18}$	158	158	1.58
$n\text{-}C_{20}$	304	304	3.04
Dimethylphenol (DMP)	200	200	2.00
Dimethylaniline (DMA)	570	570	5.70
2-Octanone	314	314	3.14
2-Ethyl hexanol	300	300	3.00
Acetone[b]			

[a] Assuming a 100:1 split ratio.

[b] Solvent.

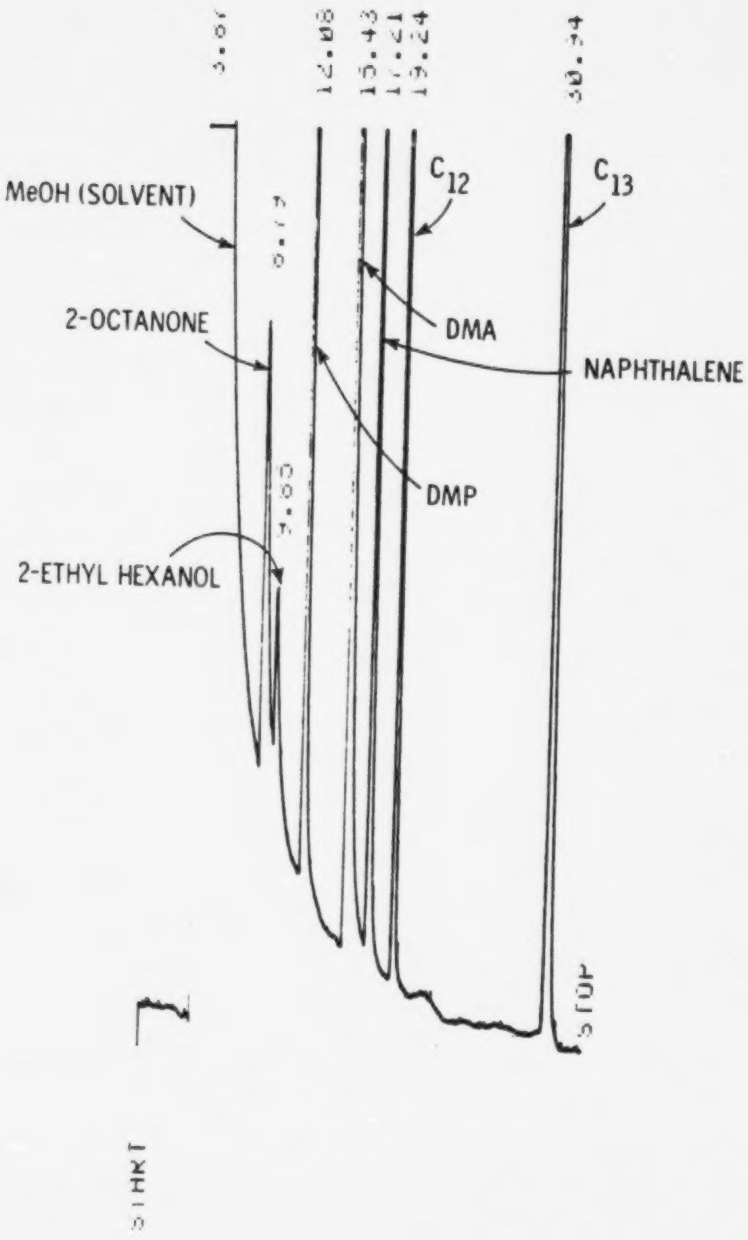


Figure 2. Chromatogram of column test mixture IIb.

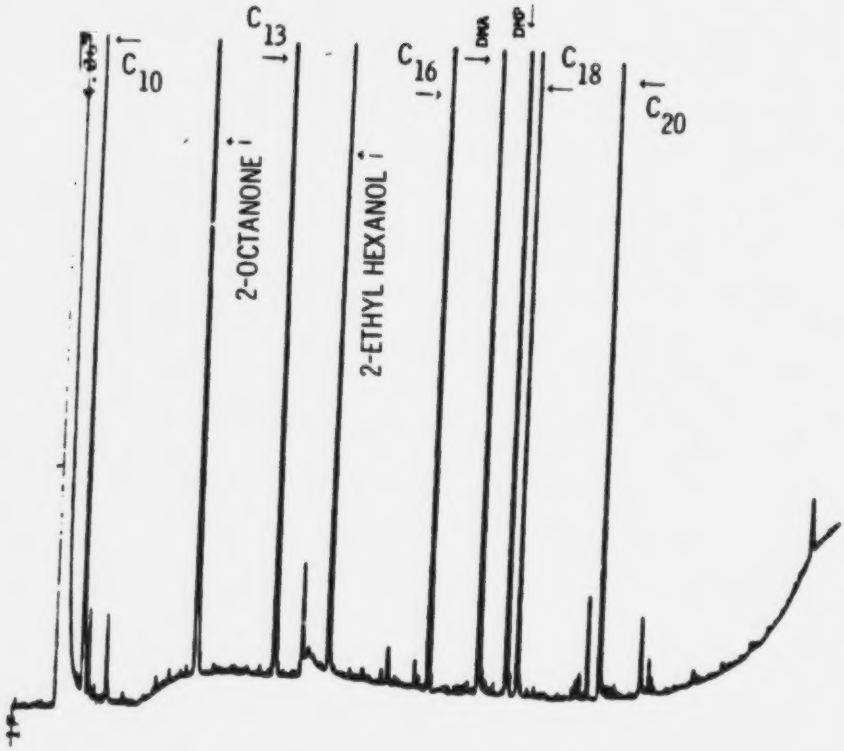


Figure 3. Chromatogram of column test mixture IIIa.

alkanes were used to characterize instrumental band-broadening effects and to calculate column parameters such as theoretical plates and separation number. Adsorption effects were indicated by naphthalene, 2-octanone, and 2-ethyl hexanol. Naphthalene tails in the presence of any metal adsorptive sites, 2-octonone tails in the presence of surfaces or interfaces which act as Lewis acids, and the alcohol (2-ethyl hexanol) indicates active siloxyl groups on glass capillary surfaces. The acid-base pair, 2,6-dimethylaniline (DMA) and 2,6-dimethylphenol (DMP), were used to determine the acidity/basicity of the capillary columns.

The chromatographic performances of the various capillary columns determined by these column test mixtures is compiled in Table 10. Generally, all of the columns demonstrated little or no tailing for the alcohol and ketone peaks unless the column was deteriorated due to age. Naphthalene was removed from the second test mixture because the capillary inlet system (to be discussed shortly) showed no major problems with adsorptive metal sites and because directly connecting the capillary columns to the GC injection port and detector eliminated metal unions. Chromatographic efficiency (as demonstrated by HETP in Table 10) was particularly good on the Carbowax 20 M WCOT column (column A) and the OV-101 fused-silica column (column D).

The ease of installing the chromatographic columns was also an important consideration. During the evaluation of the five columns all were directly connected to the GC detector and injection port. This is the "preferred" method of installing capillary columns because it eliminates active sites and dead volumes in various types of unions, such as unions made with heat-shrink Teflon tubing or low-dead volume stainless steel fittings. To install a glass column in a GC in this manner, the ends of the glass capillaries needed to be carefully straightened, cleaned, and deactivated. During the installation of the glass columns, extreme care had to be taken not to break their ends, or the procedure of straightening had to be repeated. The wide-bore glass columns were especially brittle. By comparison, the installation of the fused-silica columns was extremely simple and rapid. The outer polymeric coating and thin walls of the fused-silica columns gave them great enough flexibility and strength to be directly connected to the GC without prior preparations and without much risk of breakage.

Chromatographic Conditions

Flow rates through a capillary column are very small, ranging from ~0.7 mL/min to ~5 mL/min depending on the internal diameter of the column, the type of carrier gas, and column temperature. To get maximum chromatographic efficiency from any particular column an optimum range of flow rate exists which is described by a

TABLE 10. CHROMATOGRAPHIC PERFORMANCE OF VARIOUS CAPILLARY COLUMNS

Column	Compound	Theoretical plates, N, plates	HETP, mm/plate	Separation number		DMA/DMP ratio
				Compounds	No. of peaks	
A	n-Tridecane	~160,000	~0.3	NE	NE	1.18/1
B	n-Eicosane	~37,000	~1.1	NE	NE	NE
C	n-Eicosane	~68,000	~0.7	n-Octadecane &n-Eicosane	48	1.31/1
D	n-Eicosane	~160,000	~0.3	n-Octadecane &n-Eicosane	39	NE
E	n-Tridecane	~74,000	~0.6	n-Dodecane &n-Tridecane	26	0.84/1

Calculations:

N, plates = $[(RT, min)/(W1/2H, min)]^2$ 5.54
HETP, mm/plate = (L, mm)/(N, plates)

KEY TO TABLE AND EQUATIONS:

NE - Not evaluated.
HETP - Height equivalent of a theoretical plate
DMA - 2,6-Dimethylaniline
DMP - 2,6-Dimethylphenol
N - Theoretical plates
L - Column length
RT - Retention time of compound
W1/2H - Width at half height of compound

Columns:

A - Carbowax 20 M wall-coated, open-tubular, glass column, ~0.25 mm ID, ~48 m long
B - Carbowax 20 M wall-coated, open-tubular glass column, ~0.50 mm ID, ~50 m long
C - Carbowax 20 M wall-coated, open-tubular, fused-silica column, ~0.20 mm ID, ~50 m long
D - OV-101 wall-coated, open-tubular, fused-silica column, ~0.20 mm ID, ~50 m long
E - SP2100 support-coated, open-tubular, glass column, ~0.50 mm ID, ~45 m long

Van Deemter plot. Such a plot, shown in Figure 4, was determined for the SP2100 SCOT column. Injections of propane were used to determine dead time at various column flow rates. By dividing the column length by the retention times of propane, the linear velocities were calculated. Analyses of column test mixture IIa were performed at each of these linear velocities. The height equivalents of a theoretical plate (HETP) were calculated for n-tridecane and plotted versus the linear velocities. An optimum in chromatographic efficiency occurs at a linear velocity of ~20 cm/sec. The relationship of linear velocity, column flow rate, split flow rate, split ratio, and GC oven temperature was investigated. These values were determined at a number of GC oven temperatures and plotted in Figure 5. This demonstrates that for a temperature programmed analysis, the linear velocity decreases as oven temperature increases, affecting the column resolution during the course of the analysis. A linear velocity of ~17 cm/sec at the upper GC temperature usually provided optimal flow rate conditions during the course of a temperature-programmed analysis. This usually corresponded to a flow rate of ~0.8 to ~1.2 mL/min at this upper temperature. At the lower temperature (0°C to 35°C) flow rates ranged from ~1.2 to ~2.0 mL/min for narrow and regular bore columns, and ~3 to ~6 mL/min for wide-bore columns. (Capillary column flow rate is controlled by column head pressure on an HP Model 5840 GC, which results in changing flow rates during temperature programming. Other instruments, however, have flow controllers which can maintain a constant, optimal flow rate throughout a temperature-programmed analysis.)

Isothermal analyses of a mixture of low boiling compounds [Standard Mixture $(GC)^2$Va] were performed at various temperatures to determine whether maintaining sub-ambient temperatures could improve chromatographic resolution. A typical chromatogram of this mixture is depicted in Figure 6. Two isothermal analyses of this mixture, at 40°C and at 5°C, are shown in Figure 7. As indicated by the resolution of 1,4-dioxane and ethylene dichloride, the analysis at 40°C provides better compound separation. The reduced chromatographic efficiency at the lower temperature was thought to be due to a combination of faster linear velocity and decreased effectiveness of the column liquid phase (in this case Carbowax 20 M), which has a lower temperature limit of 60°C. Therefore, maintaining a sub-ambient temperature for a long time (J10 min) was found not to improve chromatographic resolution. Slow temperature programming (2 to 3°C/min) from sub-ambient to higher temperatures generally produced the best chromatographic results.

Capillary Inlet System

The analytical method developed for this contract was to allow the introduction of sorbent tube samples obtained by either solvent or thermal desorption. Of course, a solvent desorbed sample

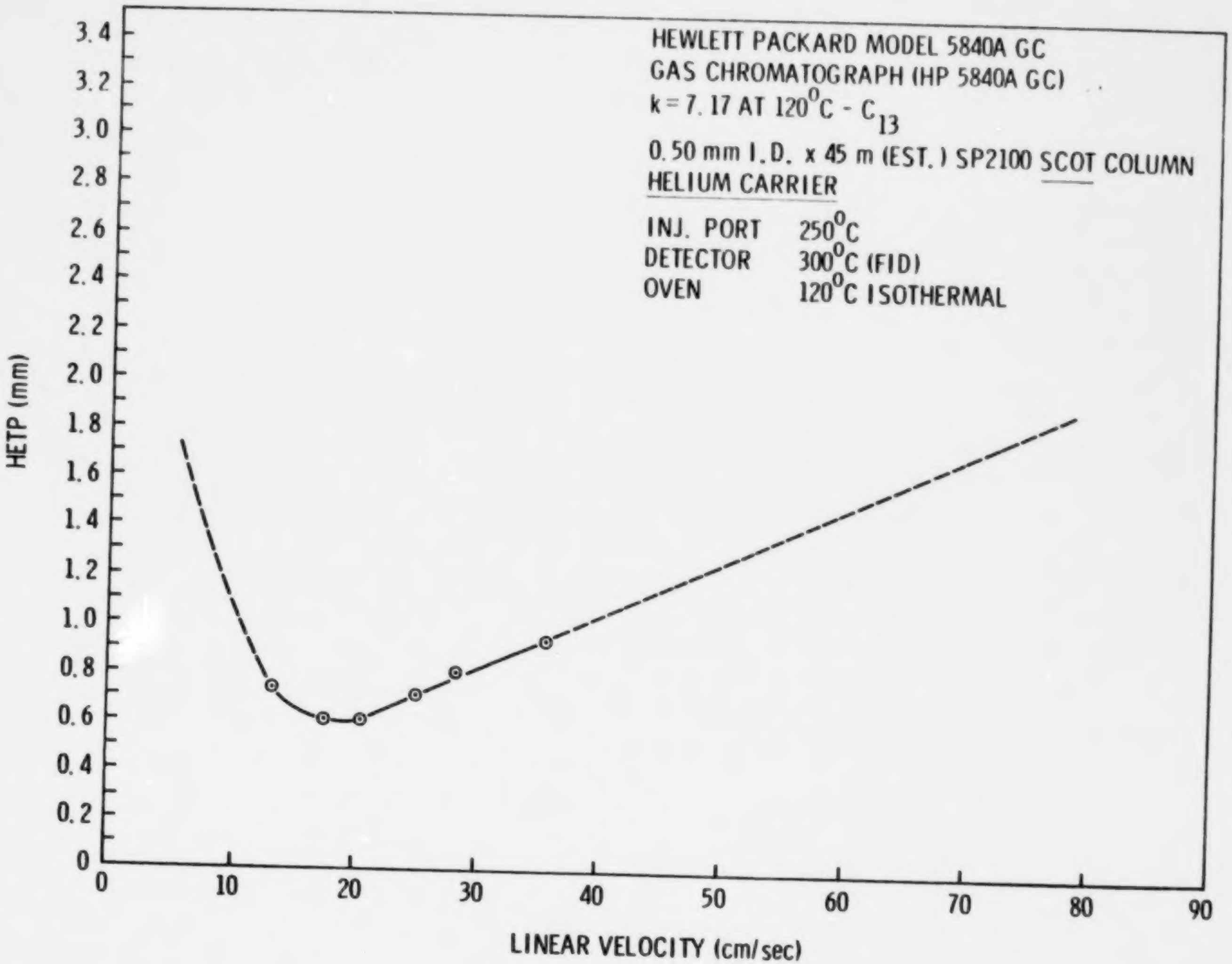


Figure 4. Van Deemter plot for analytical column.

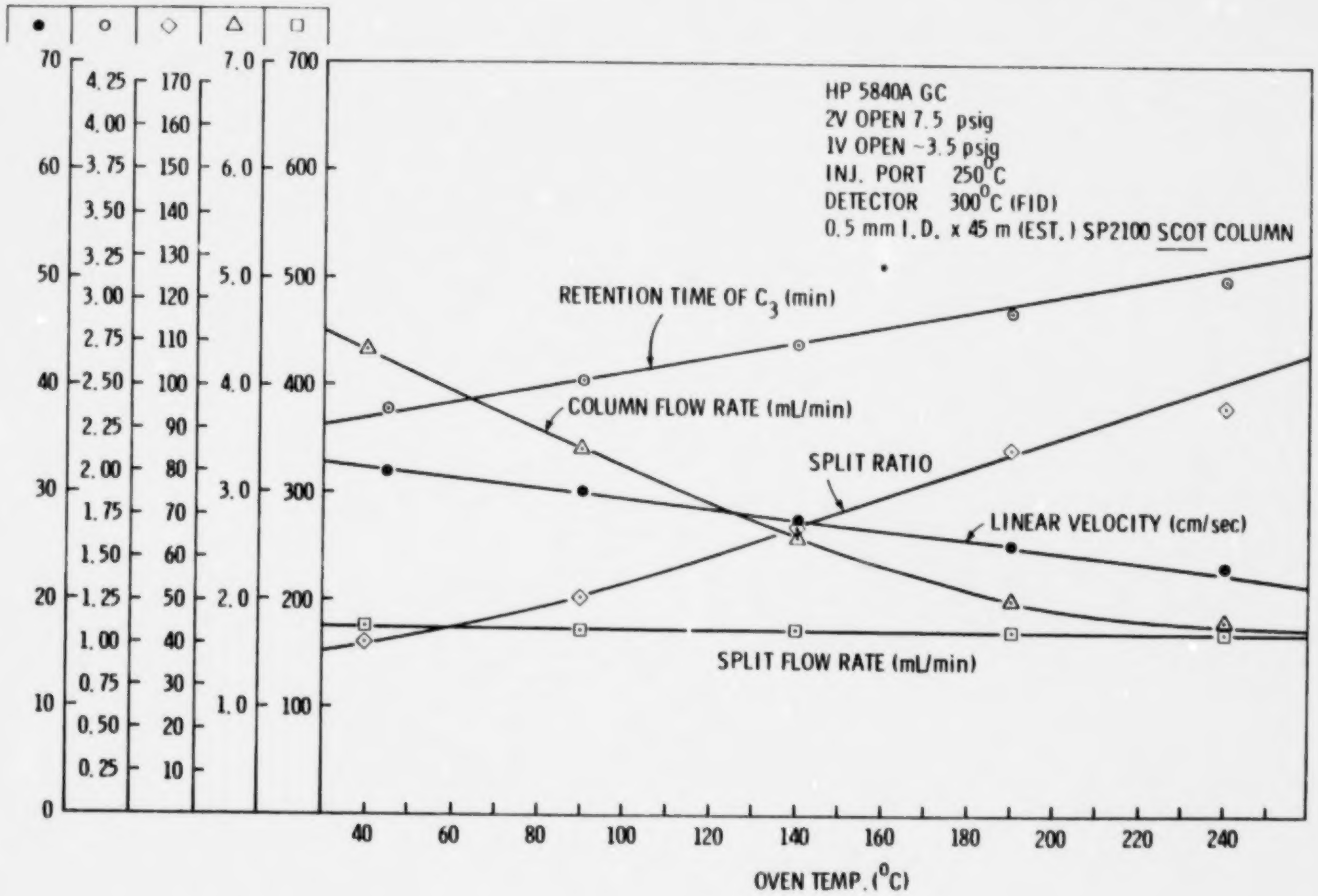


Figure 5. Effect of oven temperature on flow rates and linear velocity.

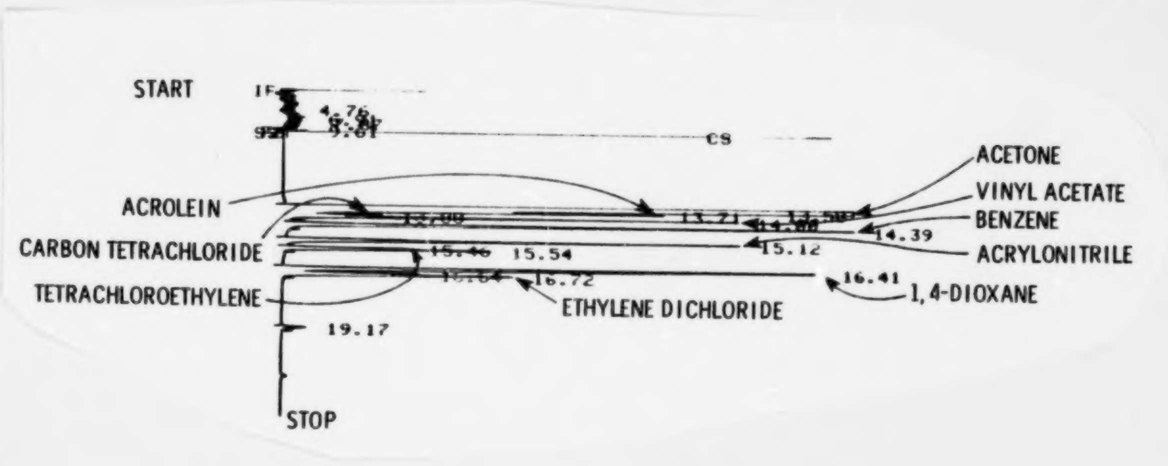
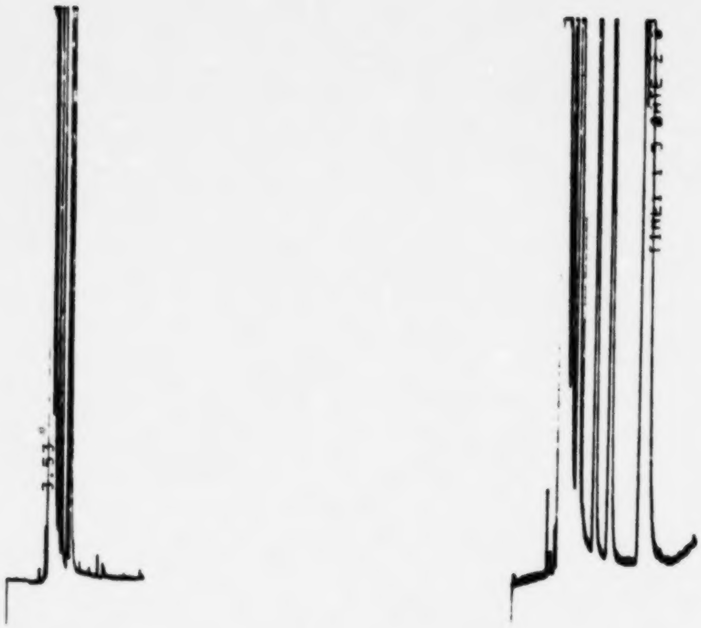


Figure 6. Typical chromatogram of Standard Mixture $(GC)^2Va$.



A. 40°C isothermal analysis

B. 5°C isothermal analysis

Figure 7. Chromatograms of Standard Mixture $(GC)^2Va$.

can be introduced into a chromatograph by syringe injection. However, a thermally desorbed sorbent sample must be reconcentrated as it is slowly desorbing from a sorbent tube, so that the entire sample can be introduced into the GC as a discrete slug. Such a discrete slug retains the chromatographic resolution capabilities of the analytical system.

An inlet system was designed and constructed to permit the thermal desorption of sorbent tubes, reconcentration of the desorbed samples in a trap, and the introduction of these samples into the capillary GC for analysis. The system was comprised of three major parts: a six-port, two-position, high-temperature valve; a sorbent-tube desorption chamber; and, a nickel capillary trap. A schematic of this system is shown in Figure 8. In the "trap" position a sorbent tube was desorbed by the tube furnace and its sample swept by the auxiliary "desorption" carrier through the valve into the nickel capillary trap, which was ∿50% submerged in liquid nitrogen. The flow out of the trap was passed through the "A" injection port to the "A" FID for monitoring trap breakthrough. When the valve was switched to the "analyze" position, simultaneously the tube furnace was cooled, the liquid nitrogen was removed from the trap, and the trap was heated. The auxiliary "purge trap" flow then swept the collected sample out of the trap and into the capillary injection port. When the capillary GC was operated in the "split" mode, most of the sample entering the injection port was vented and only a small portion entered the capillary column for chromatographic separation and analysis. In this injection mode, vented portions of samples could be recollected onto other sorbent tubes for subsequent analyses.

The auxiliary "desorption" carrier was obtained simply by splitting flow off the instrument carrier supply line. However, the auxiliary "purge trap" carrier, which was responsible for sweeping a sample from the nickel capillary trap into the capillary injection port, was controlled by the capillary injection port pneumatics. This was accomplished, as sketched in Figure 9, by installing a tee after toggle valve 1. In this configuration part of the injection port carrier would purge the capillary inlet trap and introduce samples into the injection port through a needle. The rest of the injection port carrier would purge the GC injection port in a normal manner, sweeping the introduced (through the needle) sample into the GC capillary column.

Initially, thermal desportion of sorbent tubes was accomplished by a copper tube furnace wrapped with nichrome heating wire. A thermocouple was incorporated with this furnace and the unit was wrapped with asbestos and/or glass tape insulation. The temperature of this tube furnace was controlled by a Variac, and was capable of ballistic heating and cooling. A digital voltmeter was used to measure the furnace's temperature. Although the ballistic heating and cooling capabilities of this type of furnace were found to be excellent, after constant use and manipulation,

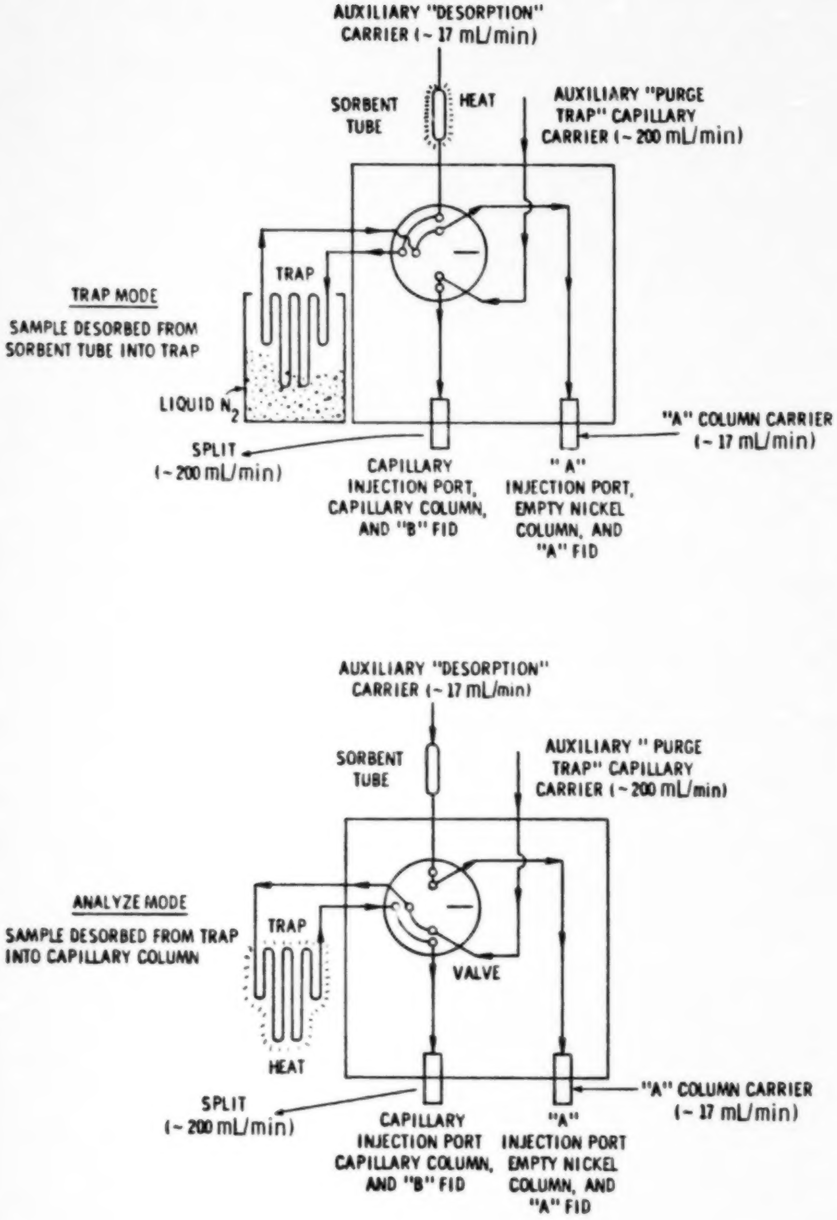

AUXILIARY "DESORPTION" CARRIER (~ 17 mL/min)
SORBENT TUBE
HEAT
AUXILIARY "PURGE TRAP" CAPILLARY CARRIER (~ 200 mL/min)
TRAP
TRAP MODE
SAMPLE DESORBED FROM SORBENT TUBE INTO TRAP
LIQUID N_2
SPLIT (~ 200 mL/min)
CAPILLARY INJECTION PORT, CAPILLARY COLUMN, AND "B" FID
"A" INJECTION PORT, EMPTY NICKEL COLUMN, AND "A" FID
"A" COLUMN CARRIER (~ 17 mL/min)
AUXILIARY "DESORPTION" CARRIER (~ 17 mL/min)
SORBENT TUBE
AUXILIARY " PURGE TRAP" CAPILLARY CARRIER (~ 200 mL/min)
ANALYZE MODE
SAMPLE DESORBED FROM TRAP INTO CAPILLARY COLUMN
TRAP
HEAT
VALVE
SPLIT (~ 200 mL/min)
CAPILLARY INJECTION PORT CAPILLARY COLUMN, AND "B" FID
"A" INJECTION PORT EMPTY NICKEL COLUMN, AND "A" FID
"A" COLUMN CARRIER (~ 17 mL/min)

Figure 8. Flow schematic of capillary inlet system.

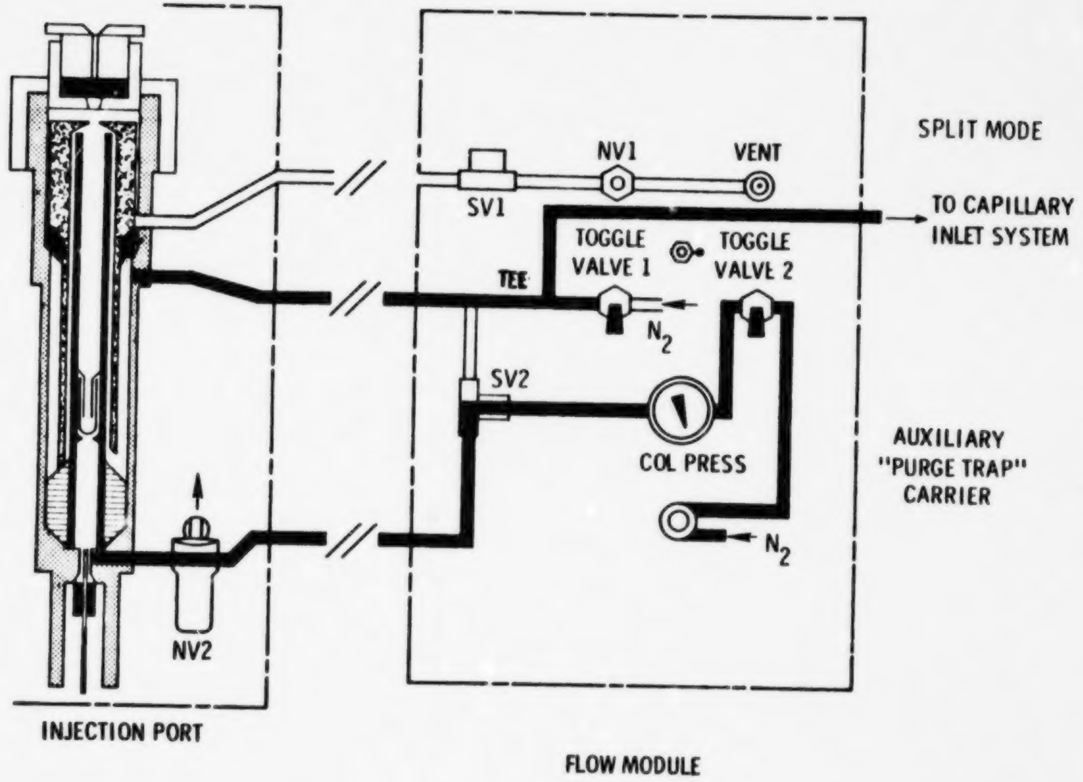

SPLIT MODE
SV1
NV1
VENT
TO CAPILLARY INLET SYSTEM
TOGGLE VALVE 1
TOGGLE VALVE 2
TEE
N_2
SV2
COL PRESS
AUXILIARY "PURGE TRAP" CARRIER
N_2
NV2
INJECTION PORT
FLOW MODULE

Figure 9. Schematic of flow pattern at the capillary GC injection port.

the insulation of the furnace would deteriorate and the thermocouple would short to the heating wire. Consequently a different, more durable, desorption chamber was designed and constructed. This desorption chamber is pictured in Figure 10. It consisted of an electrically heated aluminum block hinged in two halves with each half provided with its own thermocouple and heating element. Sorbent tubes were desorbed by being placed in the center of this device with its hinged "doors" enclosed around them. The advantages of this desorption chamber included:

- Easy mounting/dismounting of the entire unit by attachment/ detachment of its mounting bars to a ring stand;
- Ballistic heating and cooling of sorbent tubes by closing and opening the chamber's hinged doors, while maintaining the aluminum block at desorption temperatures;
- Durability due to the sturdiness of design (fragile parts embedded in the aluminum block) and simplicity of frequent manipulation (just open "doors" to change sorbent tubes); and
- Non-interference with sample analyses since the chamber was not within the desorption flow system.

Another improvement made to the capillary inlet system was the design and construction of a thermal control unit, sketched in Figure 11. This unit could accommodate all of the heating requirements of the capillary inlet system, including power supply and thermocouple monitoring. Five voltage regulators were used to supply power to the various parts of the capillary inlet system, replacing the Variacs that were previously used to perform this function. A transformer used to heat the nickel capillary trap by electrical resistance was incorporated into the thermal control unit. The voltage regulators are controlled by on/off switches, of which two can be activated/deactivated by timing devices. Desorption of the nickel trap by resistive heating was usually controlled by one of these timers to prevent the transformer from overheating. Pilot lights were also included to indicate the status of the on/off switches and intensity indicator lamps visually displayed the voltage settings of the regulators. A pyrometer attached to a multi-position selector switch permitted the alternate monitoring of up to twelve thermocouples. A sketch of the "improved" capillary inlet system is given in Figure 12.

Another improvement to the capillary inlet system, made after and as a result of analytical method development experiments and evaluation of sorbent tubes, was a slight change in the design of the nickel capillary trap. The two trap designs are shown in Figure 13. Note that the major difference in the two designs is that the "newer" trap has zones both above and below

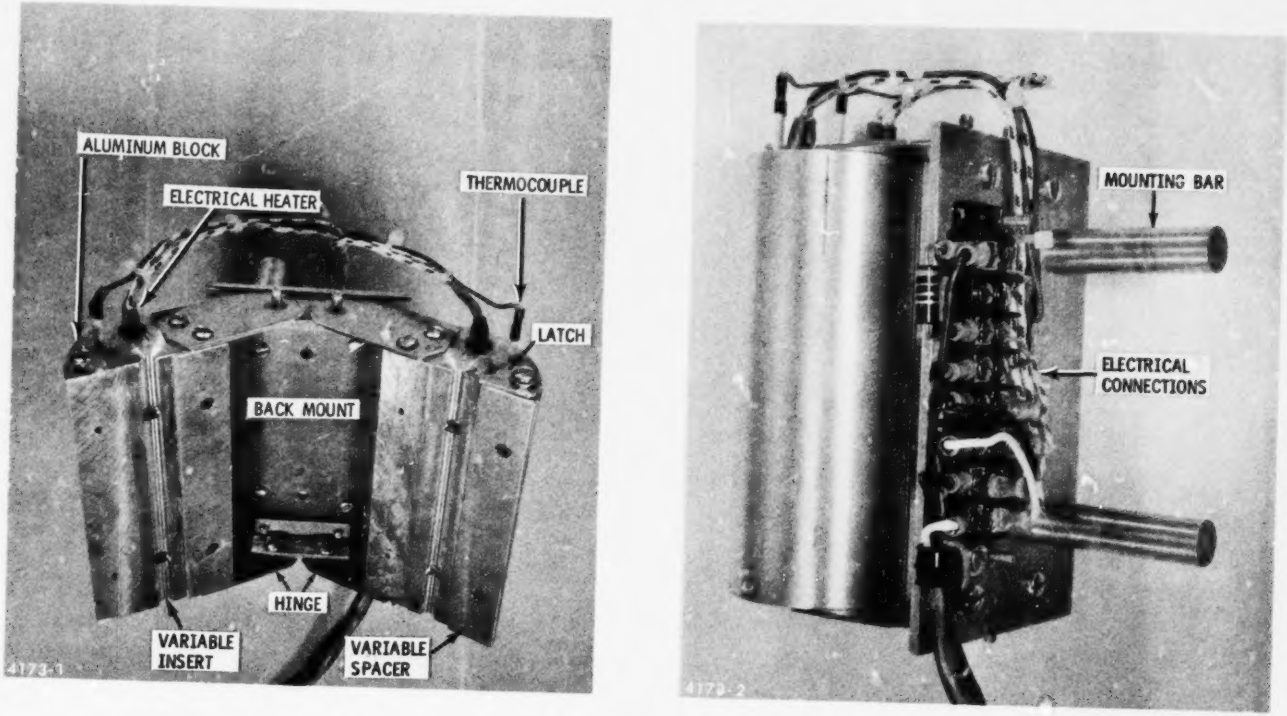

ALUMINUM BLOCK
ELECTRICAL HEATER
THERMOCOUPLE
LATCH
BACK MOUNT
HINGE
VARIABLE INSERT
VARIABLE SPACER
4173-1
MOUNTING BAR
ELECTRICAL CONNECTIONS
4173-2

Figure 10. Front and rear view photograph of new, durable capillary inlet system desorption chamber.

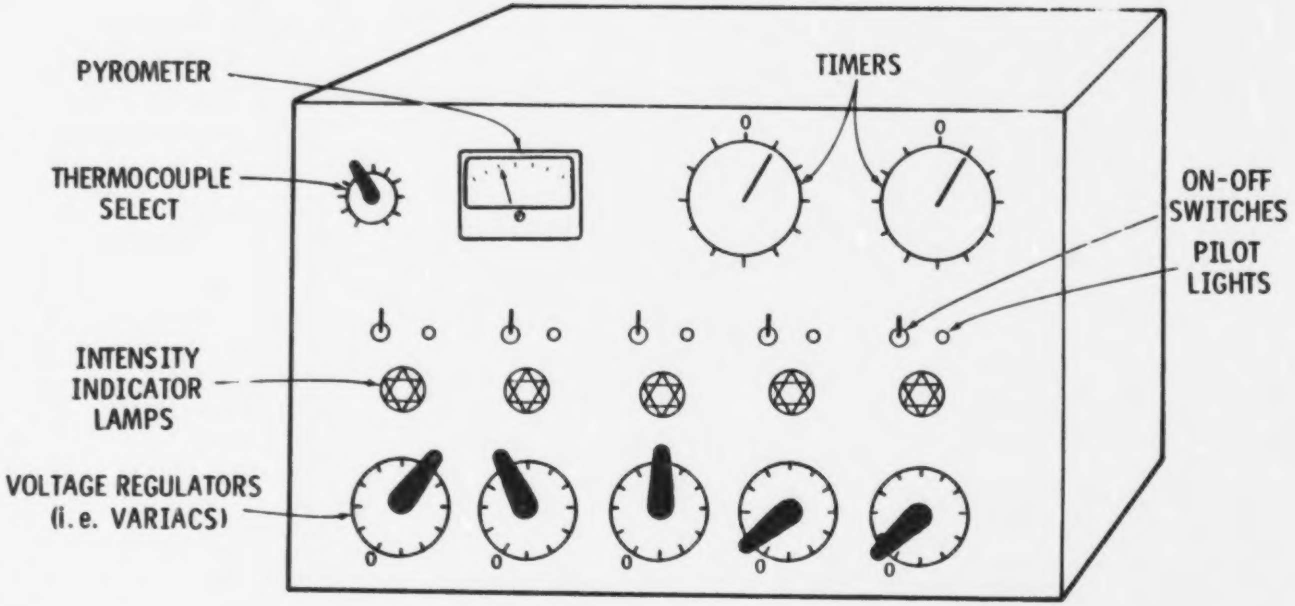
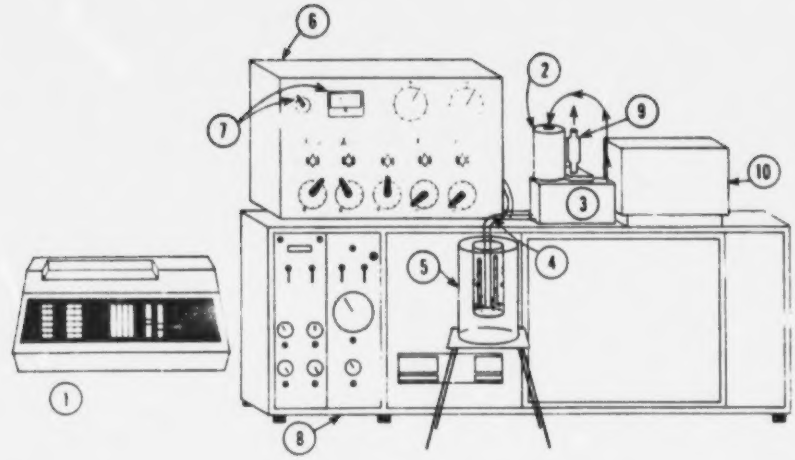

PYROMETER
TIMERS
THERMOCOUPLE SELECT
ON-OFF SWITCHES
PILOT LIGHTS
INTENSITY INDICATOR LAMPS
VOLTAGE REGULATORS (i.e. VARIACS)
0

Figure 11. Sketch of capillary inlet system thermal control unit.



① HEWLETT-PACKARD MODEL 5840A GC WITH GLASS CAPILLARY OPTION

② TUBE DESORPTION CHAMBER (OVEN)

③ HEATED VALVE OVEN-CONTAINING 6-PORT, 2-POSITION, LOW DEAD VOLUME VALVE

④ 1-METER, Ni CAPILLARY TRANSAXIAL TRAP

⑤ DEWAR CONTAINING LIQUID N_2 FOR COOLING CAPILLARY TRAP

⑥ THERMAL CONTROLLER FOR INSTANT HEATING OF CAPILLARY TRAP, HEATING DESORPTION CHAMBER HEATING VALVE, ETC.

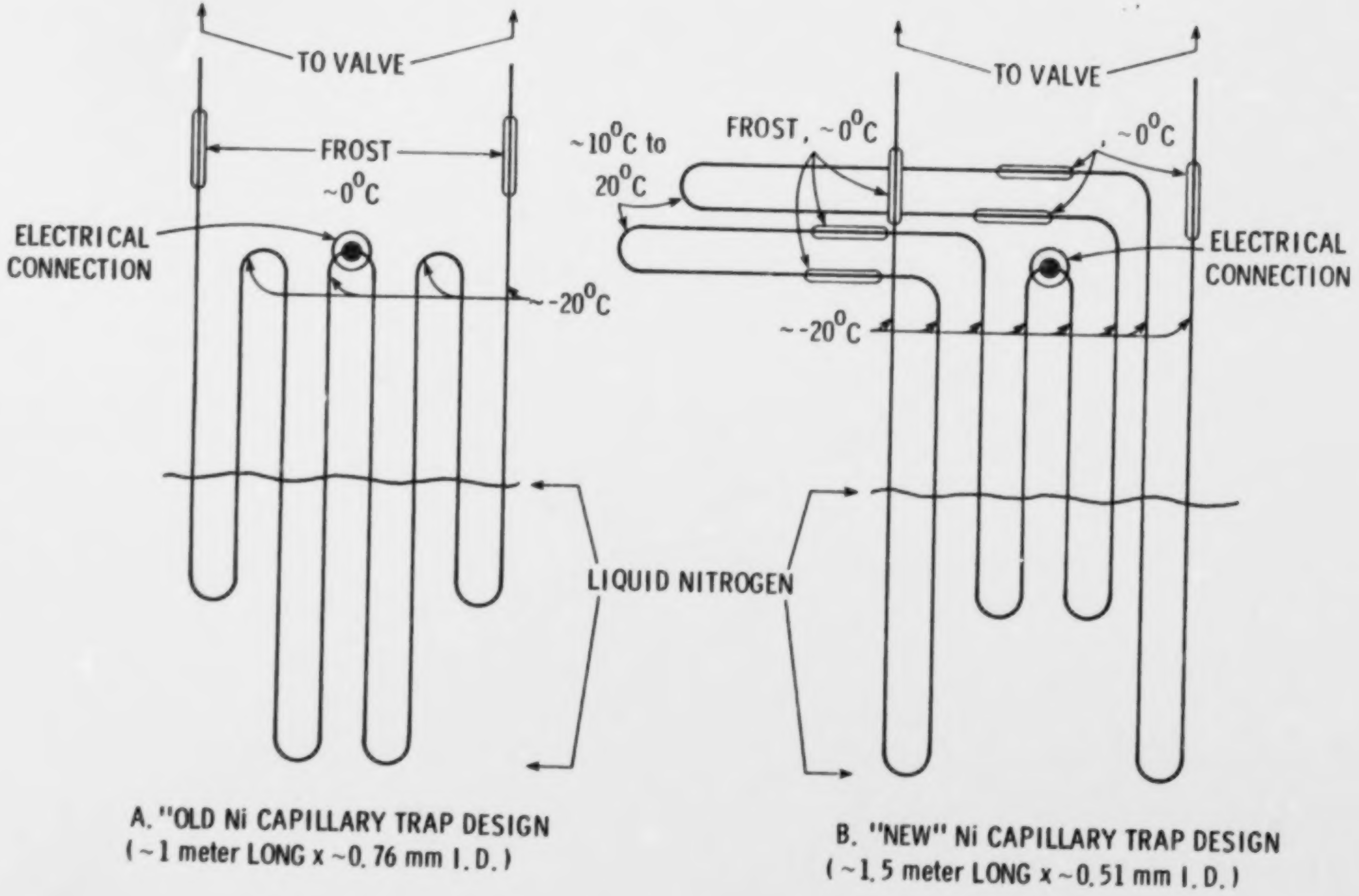
⑦ PYROMETER FOR TEMPERATURE READINGS WITH MULTI-POSITION SELECTOR

⑧ FLOW CONTROLLERS AND SPLIT CONTROLLER

⑨ RECOLLECTION VENT WITH TUBE

⑩ DETECTOR ADAPTABLE TO FID, N-P FID, GLASS JET FID

Figure 12. Capillary GC with capillary inlet system.


TO VALVE
FROST
~0°C
ELECTRICAL CONNECTION
~-20°C
LIQUID NITROGEN
~10°C to 20°C
FROST, ~0°C
TO VALVE
, ~0°C
ELECTRICAL CONNECTION
~-20°C

A. "OLD Ni CAPILLARY TRAP DESIGN
(~1 meter LONG x ~0.76 mm I.D.)

B. "NEW" Ni CAPILLARY TRAP DESIGN
(~1.5 meter LONG x ~0.51 mm I.D.)

Figure 13. Comparison of trap designs and their temperature zones during cryogenic sample reconcentration.

0°C during cryogenic sample reconcentration. This was found to reduce the problem of cryogenic trap breakthrough due to the presence of significant levels of water in samples.

The effect of this capillary inlet system on the chromatographic performance of the analytical system was evaluated by analyzing samples of the column test mixtures previously described. Immediately prior to installing the capillary inlet system on the GC, a test mixture would be analyzed to provide a basis for comparing results. Once the system was installed and demonstrated to be free of leaks, samples of the column test mixture were injected into the inlet system. These injections were either made into a stainless steel injection oven (installed in place of the sorbent tube desorption chamber) or through a tee into an empty glass tube enclosed by the desorption chamber (Figure 14). These samples were then cryogenically reconcentrated in the nickel trap before being introduced into the GC. The results of these evaluations are given in Table 11. The reproducibility of results for several injections of Standard Mixture Va (Figure 6) was also evaluated. Injections were made through a tee into a heated empty glass tube (Figure 14). Tables 12 and 13 summarize the results obtained. Overall, the capillary inlet system appeared to perform very well. Reproducibility for standards was reasonably good, the effect on chromatographic efficiency was slight, and no noticable difference in peak shapes were noted for any of the twenty selected compounds or the compounds in the column test mixtures.

Injection Mode

In order to detect between 1 and 100 parts per trillion concentrations of various compounds in ambient air, one must be able to collect at least 10 ng of a compound and then detect this amount (10 ng) or less during sample analysis. To obtain maximum sensitivity for an analysis, the entire sample contained on a sorbent tube should be introduced into the capillary column (after cryogenic reconcentration) by using the "splitless" injection mode. However, such a "one-shot" analysis does not permit a sorbent tube sample to be split and part recollected on another sorbent tube for additional analyses. Therefore, analytical sensitivity must be weighed against the requirement for multiple sample analyses for any application.

The flame ionization detectors of the Hewlett-Packard Model 5840 GC were estimated to have a detection limit of 0.01 ng to 1 ng for most compounds. Therefore most laboratory evaluations were conducted with the GC in the "split" injection mode, usually with a split ratio of 100 to 1. The "splitless" mode of sample introduction, however, was briefly investigated to evaluate the performance of the analytical system under these conditions. Two problems were noted. One was the analytical interference of the solvent with the compounds of interest in standard

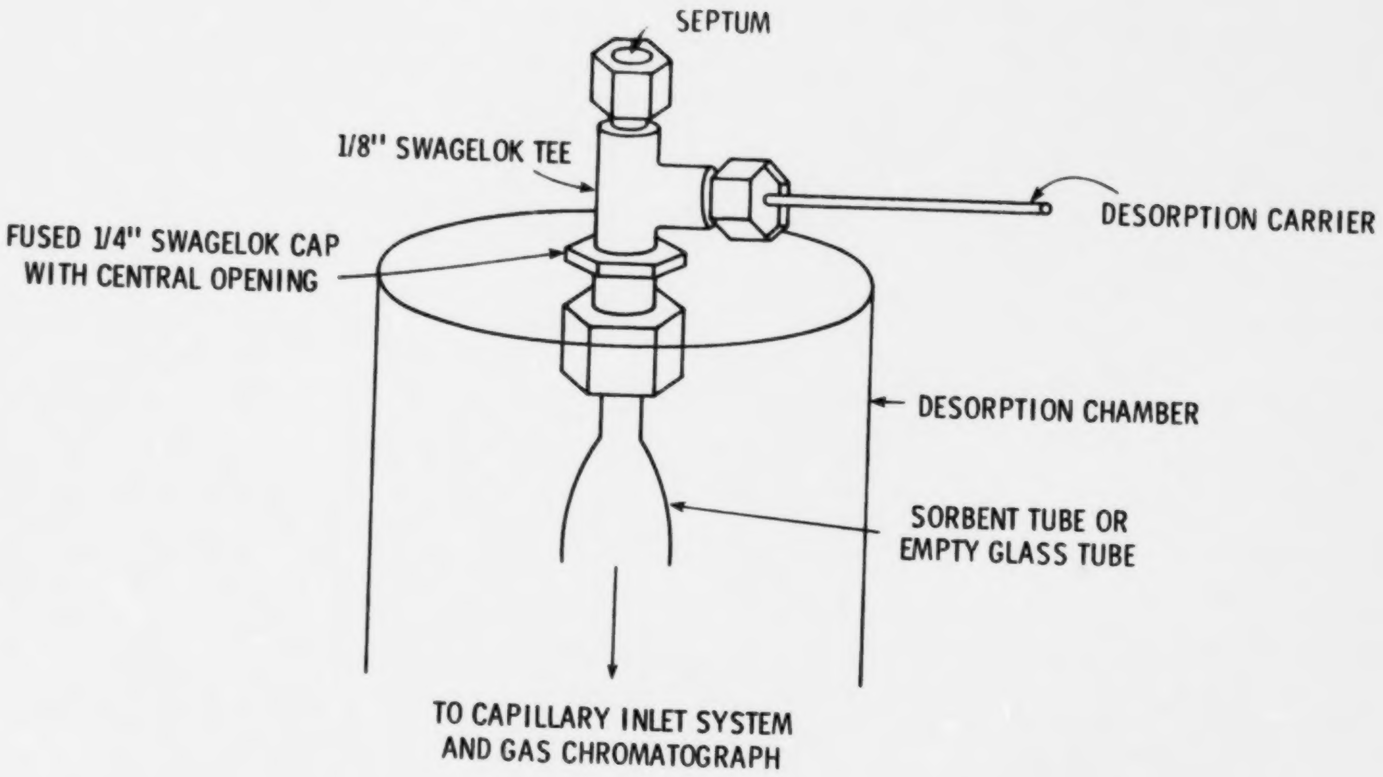

SEPTUM
1/8" SWAGELOK TEE
DESORPTION CARRIER
FUSED 1/4" SWAGELOK CAP
WITH CENTRAL OPENING
DESORPTION CHAMBER
SORBENT TUBE OR
EMPTY GLASS TUBE
TO CAPILLARY INLET SYSTEM
AND GAS CHROMATOGRAPH

Figure 14. Injection system with modified septum tee.

TABLE 11. EFFECT OF CAPILLARY INLET SYSTEM ON THE CHROMATOGRAPHIC PERFORMANCE OF VARIOUS CAPILLARY COLUMNS

Inlet system	Trap design	Column	Compound	Theoretical plates, N, plates	HETP, mm/plate
No		A	n-Tridecane	∿160,000	∿0.3
Yes	"Old"	A	n-Tridecane	∿84,000	∿0.6
No		D	n-Octadecane	∿150,000	∿0.3
Yes	"New"	D	n-Octadecane	∿53,000	∿0.9
No		E	n-Tridecane	∿74,000	∿0.6
Yes	"Old"	E	n-Tridecane	∿68,000	∿0.7

Calculations:

N, plate = [(RT, min)/(W1/2H, min)]^2 5.54
HETP, mm/plate = (L, mm)/(N, plates)

KEY TO TABLE AND CALCULATIONS:

HETP - Height equivalent of a theoretical plate
N - Theoretical plates
RT - Retention time of compound
W1/2H - Width at half height of compound
L - Column length

Columns:

A - Carbowax 20 M wall-coated, open-tubular, glass column, ∿0.25 mm ID, ∿48 m long
D - OV-101 wall-coated, open tubular, fused-silica column, ∿0.20 mm ID, ∿50 m long
E - SP2100 support-coated, open-tubular, glass column, ∿0.50 mm ID, ∿45 m long

TABLE 12. REPRODUCIBILITY OF RETENTION TIMES

Compound	Retention times, min[a]						Statistics	
	Run #468	Run #469	Run #470	Run #471	Run #472	Run #473	Mean	RSD[b], %
Acetone (solvent)	3.60	3.60	3.60	3.59	3.58	3.58	3.59	0.3
Acrolein	3.74	3.74	3.75	3.73	3.72	3.71	3.73	0.4
Carbon tetrachloride	3.92	3.92	3.92	3.90	3.89	3.88	3.91	0.5
Vinyl acetate	4.05	4.05	4.05	4.03	4.01	4.00	4.03	0.6
Benzene	4.46	4.46	4.45	4.43	4.41	4.39	4.43	0.6
Acrylonitrile	5.23	5.23	5.21	5.17	5.14	5.12	5.18	0.9
Tetrachloroethylene	5.66	5.67	5.65	5.60	5.57	5.54	5.62	0.9
1,4-Dioxane	6.58	6.58	6.59	6.50	6.47	6.41	6.52	1.1
Ethylene dichloride	6.92	6.92	6.88	6.82	6.77	6.72	6.84	1.2

[a] The 10 min reconcentration time is subtracted.

[b] Relative standard deviation.

TABLE 13. REPRODUCIBILITY OF AREA INTEGRATIONS

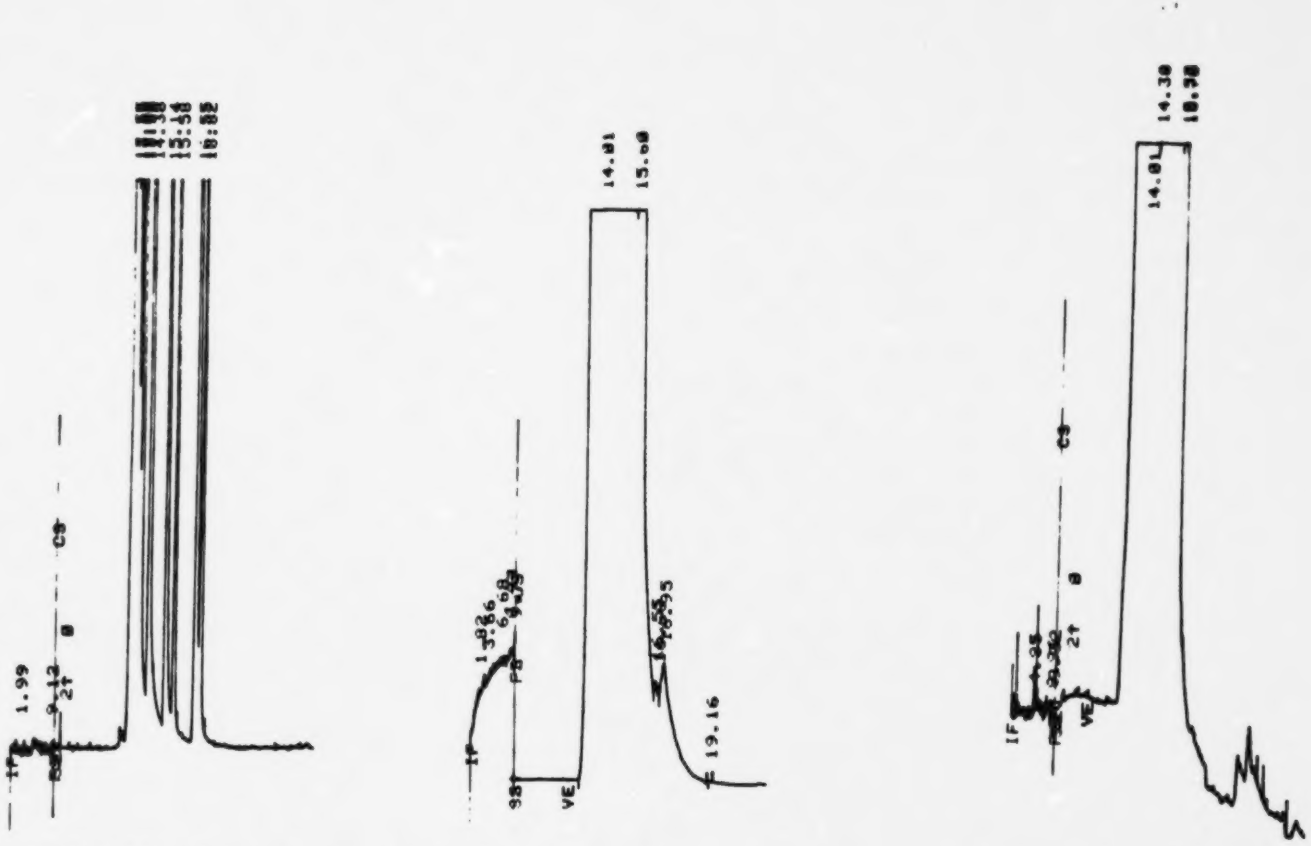
Compound	Area integrated, computer counts						Statistics					
							Corrected for injection size		Corrected for area of solvent		No correction	
	Run #468	Run #469	Run #479	Run #471	Run #472	Run #473	Mean	RSD[a], %	Mean	RSD[a], %	Mean	RSD[a], %
Acetone (solvent)	1,409,000	1,390,000	1,403,000	1,372,000	1,374,000	1,339,000	1,316,163	2.9	-	-	1,381,167	1.8
Acrolein	2,340	2,352	2,277	2,404	2,328	2,378	2,237	4.8	2,380	3.3	2,347	1.9
Carbon tetrachloride	568	552	584	605	576	613	556	5.7	591	5.5	583	3.9
Vinyl acetate	2,360	2,354	2,345	2,272	2,308	2,221	2,201	2.9	2,341	0.8	2,310	2.4
Benzene	7,328	7,236	7,348	7,164	7,168	6,998	6,868	2.8	7,305	0.3	7,207	1.8
Acrylonitrile	2,535	2,469	2,554	3,199	3,220	3,130	2,722	14.7	2,895	14.3	2,851	12.8
Tetrachloroethylene	992	941	966	1,178	1,109	1,055	993	11.3	1,055	9.9	1,040	8.8
1,4-Dioxane	5,577	5,519	5,602	5,444	5,449	5,328	5,228	2.7	5,561	0.3	5,487	1.8
Ethylene dibromide	1,250	1,216	1,307	1,496	1,500	1,332	1,288	11.0	1,370	9.9	1,350	9.0

[a] Relative standard deviation.

solutions. This is demonstrated in Figure 15 for Standard Mixture $(GC)^2Va$ (Figure 6). The other problem was the tremendous increase (~100 fold) in the level of background interferences. Therefore, if instrumental sensitivity is sufficient to permit the detection of compounds in a sample at an acceptable level (0.1 to 10 ng), the "split" mode of injection provides better analytical performance (i.e., fewer interferences) and potential multiple analyses.

RESULTS

The development of the analytical method resulted in an analytical technique which provides major analytical conditions and hardware requirements. This technique allows the separation of most of the twenty selected compounds and permits the introduction of sorbent tube samples obtained by solvent or thermal desorption. An inlet system (Figure 12), shown to efficiently and reproducibly introduce samples into a GC, provides for the introduction of samples thermally desorbed from sorbent tubes. The capillary column found to chromatograph most of the twenty selected compounds adequately (Table 7), to provide a high chromatographic efficiency (Table 10), and to allow rapid, easy installation, was on ~50 m long, ~0.2 mm ID, fused-silica, OV-101 WCOT column. A glass WCOT column of the same (OV-101) or equivalent (SP 2100) liquid phase also would probably provide similar chromatographic results, although installation would be more difficult. Fused-silica or glass WCOT columns coated with Carbowax 20M provided complimentary resolution of compounds (i.e., compounds changed elution order), but did not chromatograph high-boiling compounds. Such polar columns could be used secondarily for multiple sample analyses if further confirmation of compound identities is desired. For any analytical column, a slow temperature-programmed analysis (2 to 3°C/min), from a low temperature (0°C to 35°C) to a temperature ~30°C below the column temperature limit, provides the best analytical conditions for compound resolution. However, analysis time for high-boiling compounds with these analytical conditions is impractically large (213 min for benzo(a)pyrene). Therefore a faster temperature-programming rate (5 to 10°C/min) will probably be required to analyze "field" samples within reasonable time periods (45 to 90 min). At the upper analytical temperature, a column flow rate adjusted to obtain a linear velocity of 17 to 20 cm/sec (with helium carrier) provides optimal conditions for chromatographic efficiency. Injection of a sorbent tube sample with the GC in the "split" injection mode permits recollection of the split portion for multiple analyses and keeps background interferences to a minimum. However, this injection mode reduces analytical sensitivity and its ("split" injection) advantages must be weighed against sensitivity requirements.



A. 200:1 Split of Standard Mixture $(GC)^2$ Va.

B. Splitless injection of Standard Mixture $(GC)^2$ Va.

C. Splitless injection of Standard Mixture $(GC)^2$ Va 100-fold dilution.

Figure 15. Chromatograms of Standard Mixture $(GC)^2$Va comparing split and splitless modes of injection.

In the actual analyses of field samples certain changes were made in the analytical technique owing to either improvement or convenience of operation with the GC/MS system, or conditions/properties of the particular samples (e.g., high water content). These changes are described in detail in Section 11. Most notable among these was the use of splitless injection and capillary direct injection techniques and the modification of the GC temperature program for samples with high water content. The following summarizes the preferred technique used for the analyses:

Instrument: Hewlett-Packard Model 5985B GC/MS

Column: Methyl Silicone (OV101, SE-30, SP2100 or equivalent) capillary (fused silica or glass), 50 m, 0.2-0.25 mm ID.

Temperature Program: Subambient (-30°C) during tube desorption. Rapid rise (~30°C/min) to 0°C. More gradual temperature rise (~8°C/min) to ~30° below upper temperature limit of column.

Inlet System: Nutech Model 320 thermal desorption system, capillary direct coupling (with desorption chamber shown in Figure 10).

Mass Spectrometer: Scan Mode

SECTION 7

DEVELOPMENT OF THE SAMPLING SYSTEM

OBJECTIVE

A portable miniature collection system was to be developed so that a wide variety of atmospheric pollutants, especially the twenty selected potential carcinogens, could be collected effectively for subsequent laboratory analyses. This system was to incorporate a combination of solid sorbents of complimentary adsorption characteristics. As presented in a previous report [1], the sorbent materials selected were Tenax-GC, Porapak R, and Ambersorb XE-340. Cartridges containing these sorbents were to be included in a sampling system fabricated for the easy, efficient collection of ambient air samples.

INSTRUMENTATION

The analytical system, described in Section 6, was developed concurrently with the development and evaluation of the sampling technique. This analytical system was used in a variety of configurations (particularly with various capillary columns) for the analyses of sorbent cartridges. The analyses of the sorbent cartridge were measured against analytical standards to allow the comparison of results obtained with the various analytical configurations. Vaporous samples of the more volatile compounds of interest were produced with the Sample Generation System described in Appendix B. These samples were "known" artificial atmospheric environments which could be sampled with sorbent cartridges. This allowed the evaluation of the sorbent cartridges under somewhat realistic sampling conditions.

EVALUATION

Design Criteria

The first step in the development of the portable miniature collection system was to evaluate the basic design options and criteria of an air sampling system. The most basic sorbent sampling system (Figure 16) is comprised of only four major elements: a particulate filter, usually placed at the inlet of a system; a cartridge to contain the sorbent material; a pump to draw the air sample; and, tubing to connect the filter, cartridge,

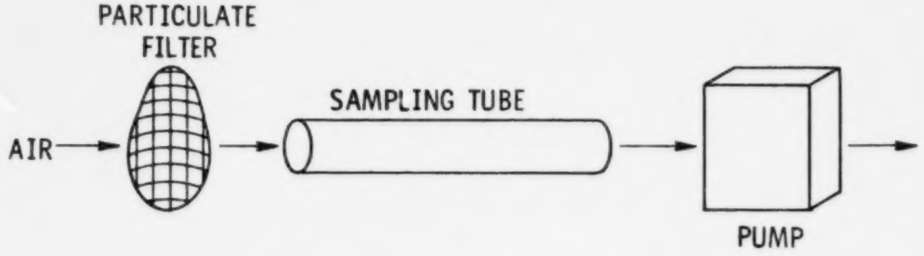


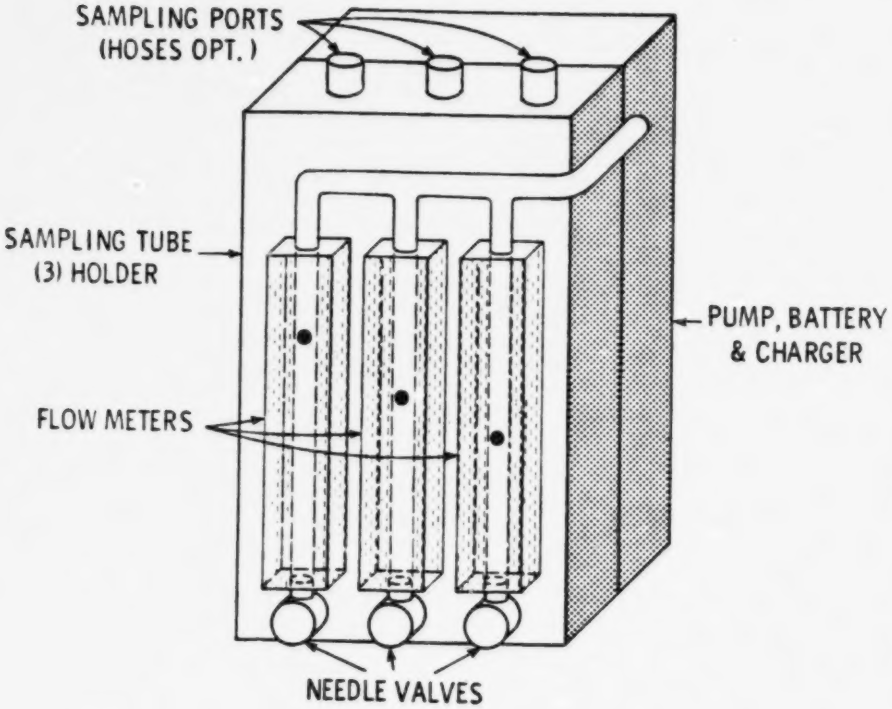
Figure 16. Basic sampling system.

and pump. However, specific parameters such as flow rate, cartridge design, and materials of construction need to be adapted to the specific sampling application. Therefore, these four basic elements and various sampling parameters were assessed with respect to this project.

Since some of the compounds of interest, such as acrylonitrile and benzyl chloride, tended to be reactive, inert materials were chosen for the fabrication of the sampling system. Silanized pyrex glass was the material selected for the sorbent cartridges. Similarly, silanized pyrex glass wool was chosen for containing the sorbents within cartridges and for use as a particulate filter. Interconnecting tubing was preferably inert, flexible, and non-contaminating, so Teflon was selected as the most suitable material. Stainless steel was chosen for connecting fittings.

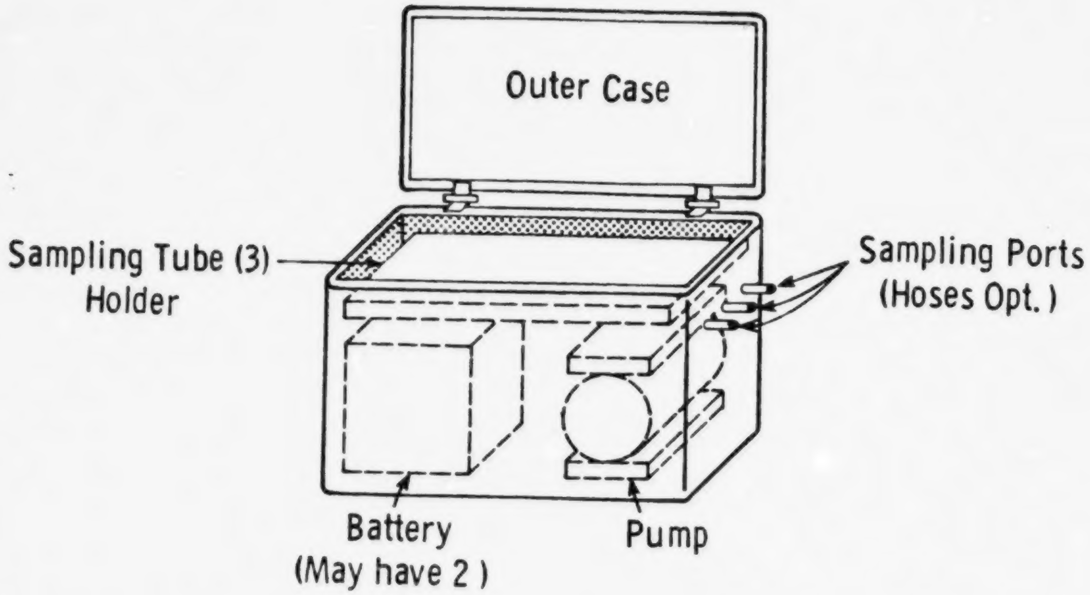
Another area of consideration was the size, weight, cost, and durability of the sampling system versus the sampling capabilities of the pump. Two collection system designs were tentatively considered for this project. Sketches of these two designs are given in Figures 17 and 18 along with descriptions of their most outstanding features. Figure 17 depicts a small personnel sampler while Figure 18 depicts a larger, heavier, "desk-top" model. While the smaller system offers the advantages of light weight, low cost, and convenient usage (i.e., it is portable and miniature); the larger model would be more mechanically durable and have greater operational capabilities (i.e., higher flow rates).

Combining the three selected sorbent materials within a single sampling system also had to be contemplated. In a previous application for the collection of jet exhaust fumes, different sorbents were combined within a single cartridge [48]. However, the three sorbents selected for this application did not have compatible temperature limits. The temperature limit of Porapak R (250°C) is significantly less than Tenax-GC (350°C) and Ambersorb XE-340 (>400°C). Therefore, if thermal desorption was used to analyze these tubes, a low temperature would be required for sorbents combined in a single cartridge, or optimal desorption temperatures would be possible for sorbents in separate


SAMPLING PORTS
(HOSES OPT.)
SAMPLING TUBE
(3) HOLDER
PUMP, BATTERY
& CHARGER
FLOW METERS
NEEDLE VALVES

Weight	- 2.3 kg (<5 lb)
Cost	- $635 for DuPont P4000-A (pump, battery and charger only)
Size	- 2 or 3 times the size of most pocket calculators
Operational time	- ≥8 hours
Method of setting flow	- Needle valves and small flow meters
Durability problems	- Needle valves fragile and pump near max for long periods

Figure 17. Sketch and description of small personnel sampler.


Outer Case
Sampling Tube (3) Holder
Sampling Ports (Hoses Opt.)
Battery (May have 2)
Pump

WEIGHT - ∿32 lbs (∿60 if 2 batteries)
COST - ∿$385 (for case, 1 battery, charger and pump only)
SIZE - 13" (long) x 8" (wide) x 5" (deep)
OPERATION TIME - 4-6 hrs (>8 hrs with 2 batteries or wall adaptor)[a]
METHOD OF SETTING FLOW - Needle valves and flow meters or critical orifices[b]
DURABILITY PROBLEMS - Needle valves (if used) fragile

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[a] Battery may be put into a separate pack and/or a 120V line with transformer may be used to adapt this sampler to a wall socket.

[b] Due to pressure drop required at orifices the capabilities would be reduced.

Figure 18. Sketch and description of large desk-top sampler.

cartridges. The latter arrangement was chosen for investigation. The separation of sorbents into different sorbent cartridges allows the additional option of parallel or series sampling. Table 14 summarizes the properties of the sorbent materials previously evaluated for this project. Table 15 qualitatively describes the performance of the three selected sorbent materials anticipated for the two sampling modes (series and parallel), assuming the δ_m ranges given in Table 14 which were based on ∿1 g per sorbent and a sample volume of 480 L [1]. An evaluation of the two sampling modes was to be performed during laboratory development of the portable sampling system.

The relationship of atmospheric concentration, analytical detection limit, sample volumes, and sorbent capacities was investigated with respect to sampling limitations. Concentration and detection of organic compounds at atmospheric concentrations of ∿1 to ∿10 parts per trillion (ppt)[a] was set as an objective. Assuming an analytical detection limit of 10 ng, Figure 19 shows the relationship between atmospheric concentration and sample volume necessary to collect a detectable sample of benzene. The larger the volume of sample collected, the lower the atmospheric concentration which is detectable. However, there are limitations to the amount of sample that can be collected on sorbent materials. One limitation is the capacity of a sorbent or sorbent system for any particular compound. The capacities per gram of sorbent of Tenax-GC, Porapak R, and Ambersorb XE-340 for benzene are also shown in Figure 19. As indicated, if a sample is collected at a rate of 1-3 L/min for 8 hours, the capacities of 1 gram of Tenax and Porapak R for benzene would be exceeded. Benzene would "break through" sorbent cartridges containing 1 g of these sorbents before being concentrated to an analytically detectable level. However, the capacity of 1 g of Ambersorb XE-340 for benzene is much greater than the sample volume indicated. By collecting that sample volume, atmospheric concentrations of benzene could be detected down to ∿8 ppt with an Ambersorb cartridge and a sample volume of 480 L, or ∿2 ppt with an Ambersorb cartridge and a sample volume of 1440 L. Similar relationships between sorbent capacity, atmospheric concentration, sample volume, and analytical detection limit exist for all atmospheric pollutants. Thus, for any given sample volume, different groups of atmospheric pollutants will be concentrated to analytically detectable levels on different

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[a] $1 \text{ ppt} \times \frac{MW}{24450} = 1 \text{ ng/L}$ (in air at STP)

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[48] Brooks, J. J., D. S. West, J. E. Strobel, and L. Stamper. Jet Exhaust Analysis by Subtractive Chromatography. SAM-TR-78-37, USAF School of Aerospace Medicine, Brooks Air Force Base, Texas, Dec. 1978. 76 pp.

TABLE 14. ADSORBENT PROPERTIES CHART

Adsorbent	Temp. limit, °C	Cond. temp., °C	Des. temp., °C	Chemical composition	Major thermal decomposition products	Background level	ΔP,[a] psig[b]	Capacity	Desorption	Range of utility, in terms of δ_m
Tenax-GC (35/60 mesh)	400	320	300	2,6-Diphenyl-p-phenylene oxide	Alkyl benzene Styrene Benzene Alkyl phenols	GOOD (None detected above system background)	160	Should efficiently trap intermediately (and less) volatile compounds with slightly less affinity for polar compounds.	Very amenable to thermal desorption for intermediately (and all higher) volatile compounds.	~950->2,800
Porapak R (50/80 mesh)	250	235	150 to 220	N-Vinyl pyrrolidone	Vinyl Pyrrolidone Pyrrolidone Pyrrilidiene	After conditioning at 235°C, background upon desorbing is: POOR @ 220°C (well above system background) FAIR @ 150°C (slightly above system background)	~1.1[c]	Should efficiently trap intermediately (and less) volatile compounds with slightly greater affinity for polar compounds.	Very amenable to thermal desorption for intermediately (and all higher) volatile compounds.	~750-~1,500
Porapak N (50/80 mesh)	190	175	150	N-Vinyl pyrrolidone	Vinyl pyrrolidone Pyrrolidone Pyrrilidiene	POOR (Well above system background)	1.1	Should efficiently trap intermediately (and less) volatile compounds with slightly greater affinity for polar compounds.	Very amenable to thermal desorption for intermediately (and all higher) volatile compounds.	~750-~1,500
Ambersorb XE-340	>400	320	300	Carbonized styrene-divinyl benzene	None observed (after conditioning at 350°C + observing on GC/MS)	GOOD (None detected above system background)	0.6	Should efficiently trap highly (and all less) volatile compounds with greater affinity for polar compounds.	Questionable amenability to thermal desorption for all but highly volatile hydrocarbons.	~450-~750
SKC Activated charcoal	>400	320	300	Carbonized organics	None observed	GOOD (None detected above system background)	~0.6[c]	Should efficiently trap highly (and all less) volatile compounds with much greater affinity for polar compounds.	Questionable amenability to thermal desorption for all but highly volatile hydrocarbons.	~350-~600

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[a] Pressure drop across tapered tubes containing 1.0 g of adsorbent at a 3-liter/min flow rate.

[b] 1 psig = 6.9×10^3 Pa.

[c] Estimated.

TABLE 15. EVALUATION OF SORBENT PACKAGE FOR TWO MODES

Sorbent	Mode			
	Series		Parallel	
	Trap	Desorb	Trap	Desorb
Tenax-GC (δ_m, ∿950 to >2,800)	Quantitatively trap all low and some intermediately volatile compounds and partially (<100%) trap all other compounds.	Quantitatively desorb (almost) all compounds trapped, including those only partially trapped.	Quantitatively trap all low and some intermediately volatile compounds, and partially (<100%) trap all other compounds.	Quantitatively desorb (almost) all compounds trapped, including those only partially trapped.
Porapak R (δ_m, ∿750 to ∿1,500)	Quantitatively trap all intermediately volatile compounds passing through the Tenax, and partially (<100%) trap all other compounds passing through Tenax.	Quantitatively desorb all compounds trapped from Tenax breakthrough, including those only partially (<100%) trapped.	Quantitatively trap all low and intermediately volatile compounds, and partially (<100%) trap all other compounds.	Quantitatively desorb most of the intermediately volatile and partially trapped compounds, and partially (<100%) desorb some intermediately and low volatility compounds.
Ambersorb XE-340 (δ_m, ∿450 to ∿750)	Quantitatively trap most of the highly volatile compounds breaking through both the Tenax and the Porapak with other more volatile compounds being partially (<100%) trapped.	Quantitatively desorb most of the compounds trapped, except possibly those highly volatile compounds that border on intermediate volatility which may only partially (<100%) desorb.	Quantitatively trap all of the low and intermediately volatile compounds and most of the highly volatile compounds and partially (<100%) trap even more highly volatile compounds.	Quantitatively desorb most of the highly volatile quantitatively and partially trapped compounds, partially desorb (<100%) some intermediately (and border) volatile compounds, and not desorb (∿0%) most other compounds.

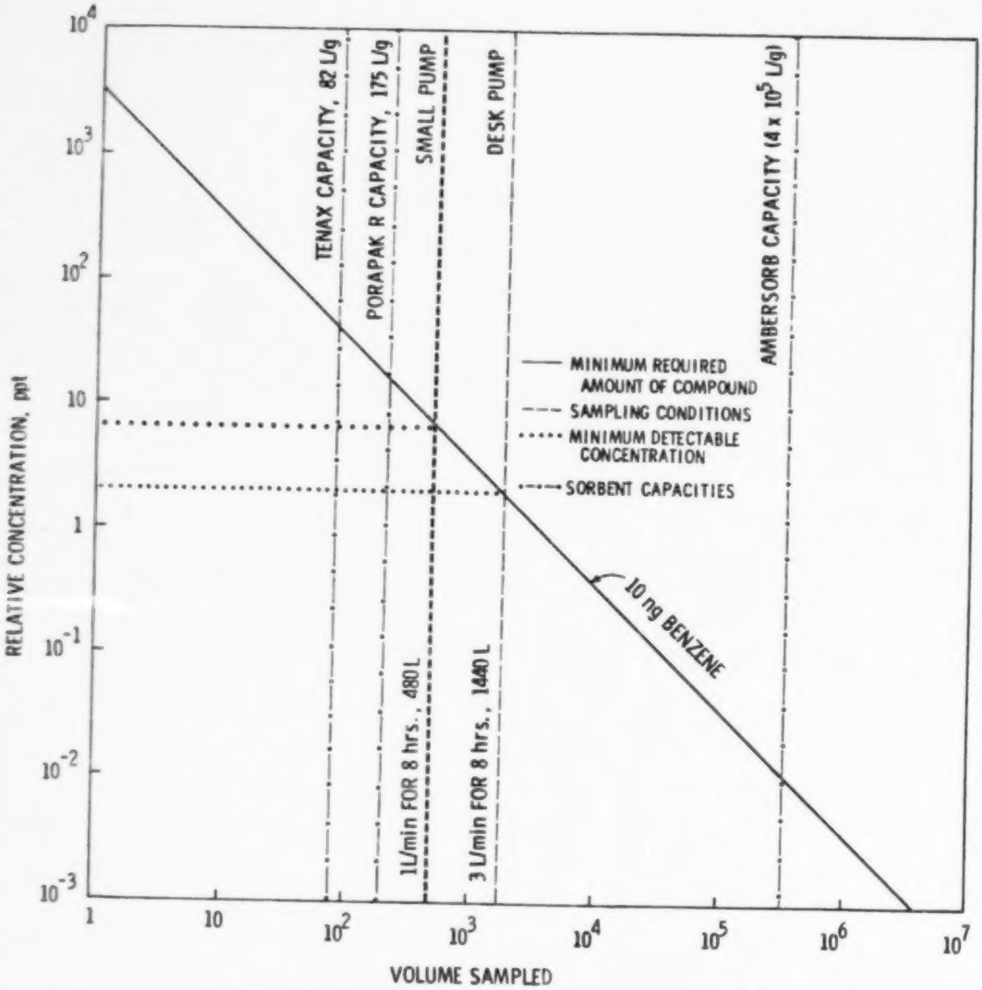

Figure 19. Relationship between concentration, volume sampled, and approximate detection limit (10 ng) for benzene with sorbent capacities superimposed (assuming 1 gram of sorbent).

sorbent materials. The lowest detectable atmospheric concentration of any particular pollutant is determined by the sample volume, as long as that volume doesn't exceed the collecting sorbent's capacity for that pollutant.

Theoretically, one could decrease the detectable atmospheric concentration of a pollutant to an infinitely small level by greatly increasing the sample volume, as long as the amount of sorbent is increased to quantitatively collect the pollutant with that larger sample volume. However, there are practical, physical limitations to this approach. The major limitation is the pressure drop across a sorbent tube system at a given flow rate and the ability of a pump to draw an air sample across that pressure drop. Glass tubes of two diameters (12 mm O.D. and 17 mm O.D.) containing 1 g of the selected sorbent materials were evaluated for their pressure drops. To estimate the total pressure drop requirements for series and parallel sampling configurations, the information given in Table 16 was used in the following equations.

Series

$$\text{Total } \Delta P = \text{Tenax Tube } \Delta P + \text{Por. R Tube } \Delta P + \text{Amb. 340 } \Delta P \qquad (1)$$

Parallel

$$\text{Total } \Delta P = [(\text{Tenax Tube } \Delta P)^{-1} + (\text{Por. R Tube } \Delta P)^{-1} + (\text{Amb. 340 } \Delta P)^{-1}]^{-1} \qquad (2)$$

The results of these calculations for different sampling configurations are given in Table 17. Note that the flow rate through each sampling tube in the parallel arrangement is only one-third of the total flow rate required through the pump. For any pump there are limits to the flow rate capable of being drawn over a given pressure drop which limits the flow rate attainable by a sampling system. The information given in Table 17 is plotted in Figures 20 and 21 superimposed upon the pressure drop versus flow rate (manufacturer's) specifications of a number of pumps. The pumps which are described in Figure 20 are small, light-weight models that are currently available on the market for miniature sampling applications. These types of pumps would be used in a small personal sampler such as sketched in Figure 17. Data on two larger, heavier pumps are given in Figure 21; these could be used in a "desk-top" sampling system as shown in Figure 18.

For a given period of time, the sample volume capable of being drawn by a pump is directly related to the pressure drop across the system in which it is incorporated. For sorbent cartridges, the pressure drop across a single cartridge is determined by the amount, type, and mesh size of the sorbent material, the diameter of the tube, the type and amount of material (e.g., glass wool)

TABLE 16. RESULTS OF PRESSURE DROP STUDIES ACROSS TWO DIAMETERS OF TAPERED GLASS SAMPLING TUBES

Sorbent material	Flow rate, ℓ/min	Pressure drop across 12 mm O.D. glass tube,		Pressure drop across 17 mm O.D. glass tube,	
		ΔP, psig[a]	ΔP, in. H_2O[a]	ΔP, psig[a]	ΔP, in. H_2O[a]
Ambersorb XE-340 (not sieved) 1.0 g	0.5	0.05	1.4	$<<0.05$	~ 0.05
	1	0.1	2.8	<0.05	<1.4
	2	0.2[b]	5.6[b]	0.1	2.8
	3	0.6[b]	16.7[b]		
Porapak N[c] 50/80 mesh, 1.0 g	0.5	0.2	5.6	0.05	1.4
	1	0.4	11.1	0.1	2.8
	2	<0.9[b]	<25.0[b]	0.25	6.9
	3	1.1[b]	30.5[b]		
Tenax-GC 35/60 mesh, 1.0 g	0.5	<0.3	<8.3	>0.05	>1.4
	1	0.55	15.3	0.15	4.2
	2	1.1	30.5	>0.25	>6.9
	3	1.6	44.4		
Three above in series	0.5	0.5	13.9	0.1	2.8
	1	0.95	26.4	0.25	6.9
	2	2.0[b]	55.5[b]	0.5	13.9
	3	3.3[b]	91.6[b]		
Tenax-GC 35/60 mesh, $\sim$2 to 3 g	0.5			0.2	5.6
	1			>0.4	>11.1
	2			~ 0.9	25.0

[a] 1 psig = 6.9×10^3 Pa; 1 in. H_2O = 2.5×10^2 Pa.

[b] Determined previously.

[c] Porapak R is approximately the same.

TABLE 17. TOTAL PRESSURE DROPS ACROSS DIFFERENT SAMPLING CONFIGURATIONS

	Sampling arrangement					
	Series			Parallel		
Flow rate through pump, ℓ/min	ΔP total (in in. H_2O^a) $= x + y + z^b$		Flow through tube, ℓ/min	ΔP total (in in. H_2O^a) $= \left[\frac{1}{x} + \frac{1}{y} + \frac{1}{z}\right]^{-1b}$		Flow through tube, ℓ/min
	12 mm O.D. tubes	17 mm O.D. tubes		12 mm O.D. tubes	17 mm O.D. tubes	
0.5	13.9	2.8	0.5	0.99	0.35	0.17
1	26.4	6.9	1	1.95	0.76	0.33
2	55.5	13.9	2	3.98	1.55	0.67
3	91.6	-	3	8.68	-	1

[a] 1 in. $H_2O = 2.5 \times 10^2$ Pa.

[b] Where x, y, and z represent pressure drops across the individual tubes.

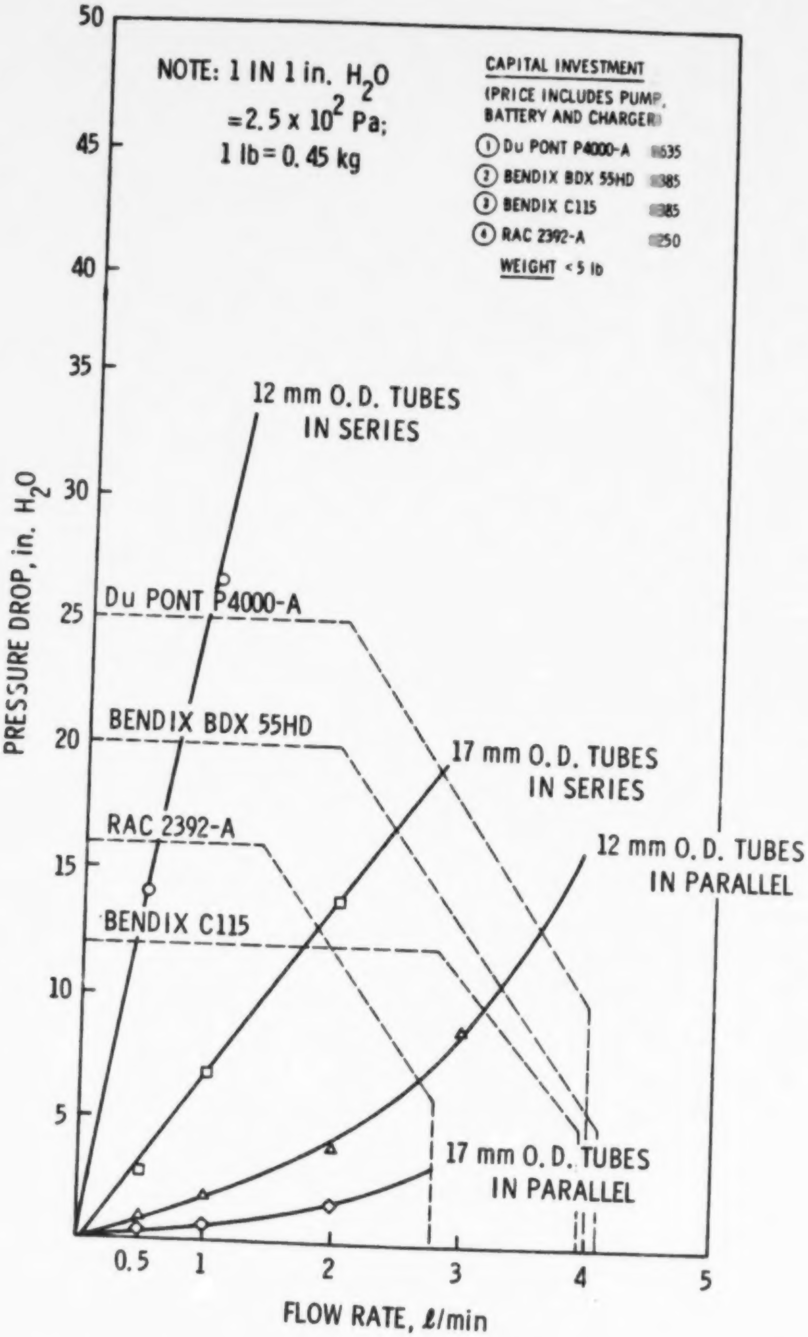

Figure 20. Plots of requirements for various sampling arrangements and the manufacturer's specifications for four miniature pumps.

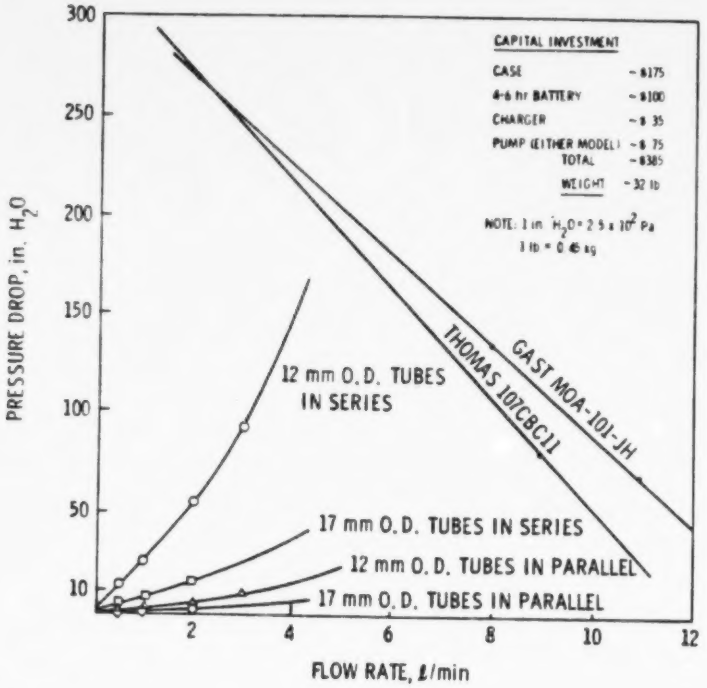

Figure 21. Plots of requirements for various sampling arrangements and the manufacturer's specifications for two large (desk-top) pumps.

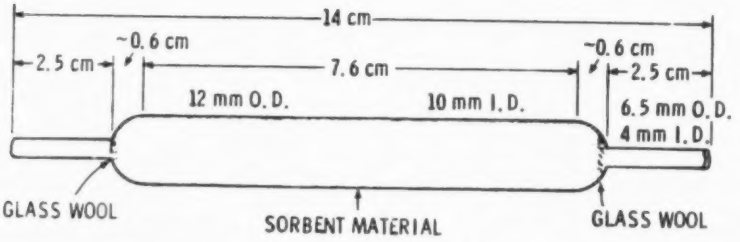
14 cm
~0.6 cm
2.5 cm
7.6 cm
~0.6 cm
2.5 cm
12 mm O.D.
10 mm I.D.
6.5 mm O.D.
4 mm I.D.
GLASS WOOL
SORBENT MATERIAL
GLASS WOOL

Figure 22. Specifications of selected sampling tube design.

used to contain the sorbent, and the flow rate through the tubes. For a multiple cartridge system, series or parallel arrangement of cartridges, interconnecting tubing, and any flow controlling valves also add to the pressure drop across a system. Therefore, minimum detectable atmospheric concentrations of pollutants are limited by both sorbent capacity and the physical design of a sampling system.

The physical design of the portable sampling system for this project was developed so that sorbent capacities were maximized and pressure drops minimized (thereby allowing any pump to draw a maximum sample volume). The first step was to select a cartridge design for the three chosen sorbent materials which would potentially allow the efficient collection of the twenty selected potential carcinogens. Pressure drop studies were conducted previously with a variety of sorbent tube designs [1]. The tube design depicted in Figure 22 was selected as offering a reasonable compromise between the requirement to have the smallest possible diameter for efficient thermal desorption (theoretically more sensitive than solvent desorption) and an acceptable pressure drop. With this design, glass cartridges could contain ~1 g of Tenax, ~1.5 g of Porapak R and ~3 g of Ambersorb. The abilities of these sorbent cartridges to collect the twenty compounds of interest was estimated by determining the molecular weight modified solubility parameters (δ_m) of the twenty selected compounds. These compounds were arranged with test compounds, previously used for sorbent material evaluations, according to increasing δ_m value [1]. The abilities of the sorbent cartridges to collect and desorb these compounds were qualitatively evaluated for a sample volume of ~480 L. The results of these evaluations are summarized in Table 18. The enclosed regions indicate compounds anticipated to be quantitatively collected and desorbed with these cartridges using this sample volume. As indicated, all of the twenty compounds of interest theoretically are effectively sampled with sorbent cartridges of this design. Therefore, this sorbent cartridge design (Figure 22) was tentatively selected for use in the Portable Miniature Collection System pending laboratory and field evaluations.

For a given set of sorbent cartridges arranged in a series or parallel configuration, a given pressure drop exists across that system of sorbent cartridges at a certain flow rate. However, as the flow rate increases, the pressure drop across the sorbent tube system also greatly increases. Therefore, although a "desk-top" sampler might be able to attain a greater flow rate across a sorbent tube system, this may not be significantly greater, in terms of analytical sensitivity, than a personal sampler. For example, as shown in Figures 20 and 21, with three 12 mm O.D. sorbent tubes combined in series, a DuPont P4000 personal pump could attain a flow rate of ~1 L/min, while or Gast MOA-101-JH pump could attain a flow rate of ~3 (or 4) L/min. These would

TABLE 18. SUMMARY OF ANTICIPATED SAMPLING CHARACTERISTICS AND CAPABILITIES

General information				Sorbent ranges of utility					
				Tenax		Por. R		Amb. 340	
Name of compound	δ_m	MW	BP, °C	Trap	Desorb	Trap	Desorb	Trap	Desorb
Methane	89	16.04	-164	0	/	0	/	0	/
Ethane	180	30.07	-88.63	0	/	0	/	0	/
Propane	282	44.09	-42.07	0	/	0	/	0	/
n-Butane	395	58.12	-0.5	0	/	0	/	0	/
Ethylene oxide[a]	489	44.05	10.7	0	/	0	/	√?	X?
n-Pentane	505	72.15	36.07	0	/	0	/	√	X?
Propylene oxide	534	58.08	34.3	0	/	0	/	√	X?
Acrylonitrile	557	53.06	78.9	0	/	0	/	√	X?
Acrolein	560[b]	56.06	52.5	0	/	0	/	√	X?
n-Hexane	629	86.17	69.0	0	/	0	/	√	X?
Benzene	719	78.11	80.1	0	/	0	/	√	X?
Vinyl acetate	769[b]	86.09	72.2	0	/	√?	/	√	X?
iso-Octane	788	114.22	99.3	0	/	√	/	√	X?
Ethylene dichloride	806	98.96	83.47	0	/	√	/	√	X?
1,4-Dioxane	881	88.10	101.5	0	/	√	/	√	X?
Ethylene glycol	906	62.07	197.2	0	/	√	X?	√	X?
Ethylene dibromide	946	187.87	131.36	√?	/	√	X?	√	X?
Styrene	969	104.14	146	√?	/	√	X?	√	X?
Succinonitrile	1,073[b]	80.09	267	√	/	√	X?	√	X
Phenol	1,176	94.11	182	√	/	√	X?	√	X
Benzyl chloride	1,253	126.58	179	√	/	√	X?	√	X
Naphthalene	1,269	128.16	217.9	√	/	√	X?	√	X
Carbon tetrachloride	1,323	153.84	76.8	√	/	√	X?	√	X
Bis-(2-chloroethyl) ether	1,402	143.02	178	√	/	√	X?	√	X
Tetrachloroethylene	1,542	165.85	121.02	√	/	√	X?	√	X
Toluene-2,4-diamine	?	122.17	280	√	/	√	X?	√	X
o-Nitroaniline	1,657[b]	138.12	284.11	√	/	√	X	√	X
m-Nitroanisole	1,684[b]	153.13	258	√	/	√	X	√	X
Phenanthrene	1,747	178.22	340.2	√	/	√	X	√	X
n-Hexadecane	1,811	226.43	287.5	√	/	√	X	√	X
1,2,4-Trichlorobenzene	2,014[b]	181.46	213	√	/	√	X	√	X
Benzidine	?	184.2	401.7(s)	√	/	√	X	√	X
4-Bromodiphenyl ether	2,616[b]	249.11	310.14	√	/	√	X	√	X
Pentachlorophenol	?	266.35	310(d)	√	/	√	X	√	X
Hexachloro-1,3-butadiene	2,783[b]	267.6	215	√	/	√	X	√	X
Di-(2-ethylhexyl) phthalate	?	?	385	√	X?	√	X	√	X
Chrysene	?	228.3	498	√	X?	√	X	√	X
Benzo(a)pyrene	?	252.3	?	√	X?	√	X	√	X

---

[a] Underlined words are the 20 selected possible and probable carcinogens.

[b] δ_m from calculated δ.

KEY:
0 - Probable trap breakthrough.
√? - Possible trap breakthrough.
√ - Quantitative trapping (with appropriate amount of sorbent).
/ - Quantitative desorption.
X? - Possibly not desorbed.
X - Probably not desirbed.
s - Sublimed.
d - Decomposes.

correspond to sample volumes of 480 L and 1440 L if sampling were conducted for 8 hours. For benzene, as shown in Figure 19, these sample volumes would theoretically permit the detection of atmospheric concentrations of benzene down to ~8 ppt and ~2 ppt. Since these theoretical concentrations are within the same order of magnitude, the portability of the small personal pumps was considered more important than the greater flow capabilities of a "desk-top" sampler. Therefore, the DuPont P4000 pumps were tentatively selected for incorporation in the Portable Miniature collection system, pending laboratory and field evaluations.

Sorbent Cartridges

Conditioning--

Generally, all commercially available sorbent materials, including the three selected for this project, contain significant levels of background contamination upon receipt as the result of production, packaging, and/or transportation. Cleanup procedures for sorbents range from short (~1 hr) thermal conditioning to exhaustive conditioning techniques involving extraction with multiple solvents and rigorous (>8 hr) thermal conditioning [49]. Since the sorbent cartridges for this project were to collect ambient air samples containing trace levels of organic compounds, an exhaustive cleanup procedure was selected. This procedure is described in Appendix A. "Blank" sorbent cartridges prepared according to these procedures and analyzed with the analytical system described in Section 6 were found to have acceptable backgrounds, as demonstrated by the chromatograms in Figure 23.

Capacity--

The ability of the sorbent cartridge to retain some of the compounds of interest was briefly investigated. As discussed in this contract's interim report [1], a chromatographic technique was used to estimate sorbent capacities which were then related to the parameter δ_m (the mathematical product of the solubility parameter and the molecular weight). This chromatographic technique is known as the "elution" method of sorbent capacity determination. Another technique of sorbent capacity determination which more realistically approximates sorbent sampling conditions is "frontal analysis". By this technique a sorbent cartridge is exposed to a given (challenge) concentration of a single compound and its effluent monitored for breakthrough. Figure 24 depicts a comparison of the two techniques. Using the Sample Generation System (Appendix B), "frontal analyses" were performed on the three types of sorbent cartridges with benzene, carbon tetrachloride,

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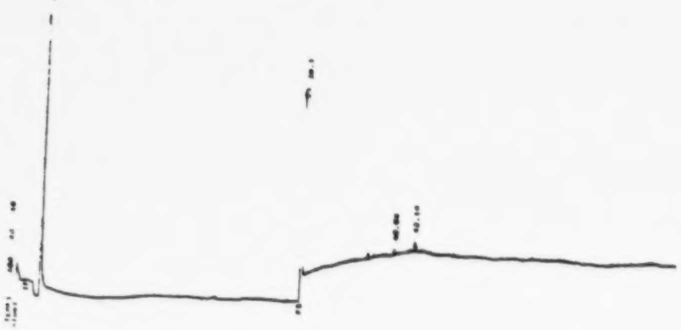
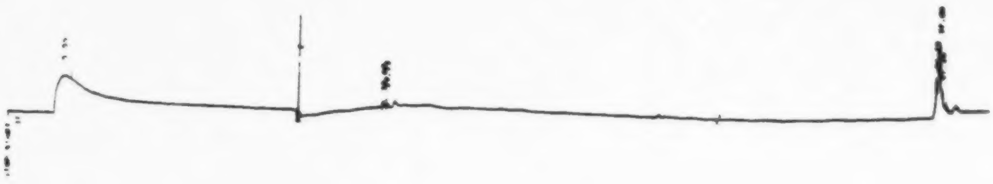
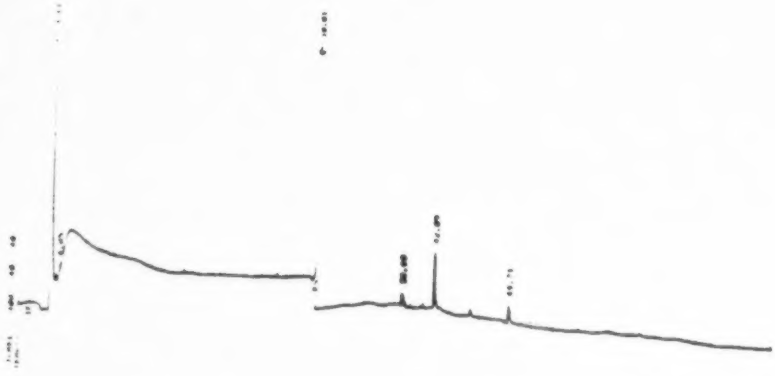
[49] Brooks, J. J., and D. S. West. Solid Sorbent Digest. Monsanto Research Corporation, Environmental Analytical Sciences Center, Dayton, Ohio, 1978. 126 pp.



A. Analysis of a blank Tenax-GC sorbent tube.



B. Analysis of a blank Porapak R sorbent tube.



C. Analysis of a blank Ambersorb XE-340 sorbent tube.

Figure 23. Backgrounds produced by desorbing blank sorbent tubes.

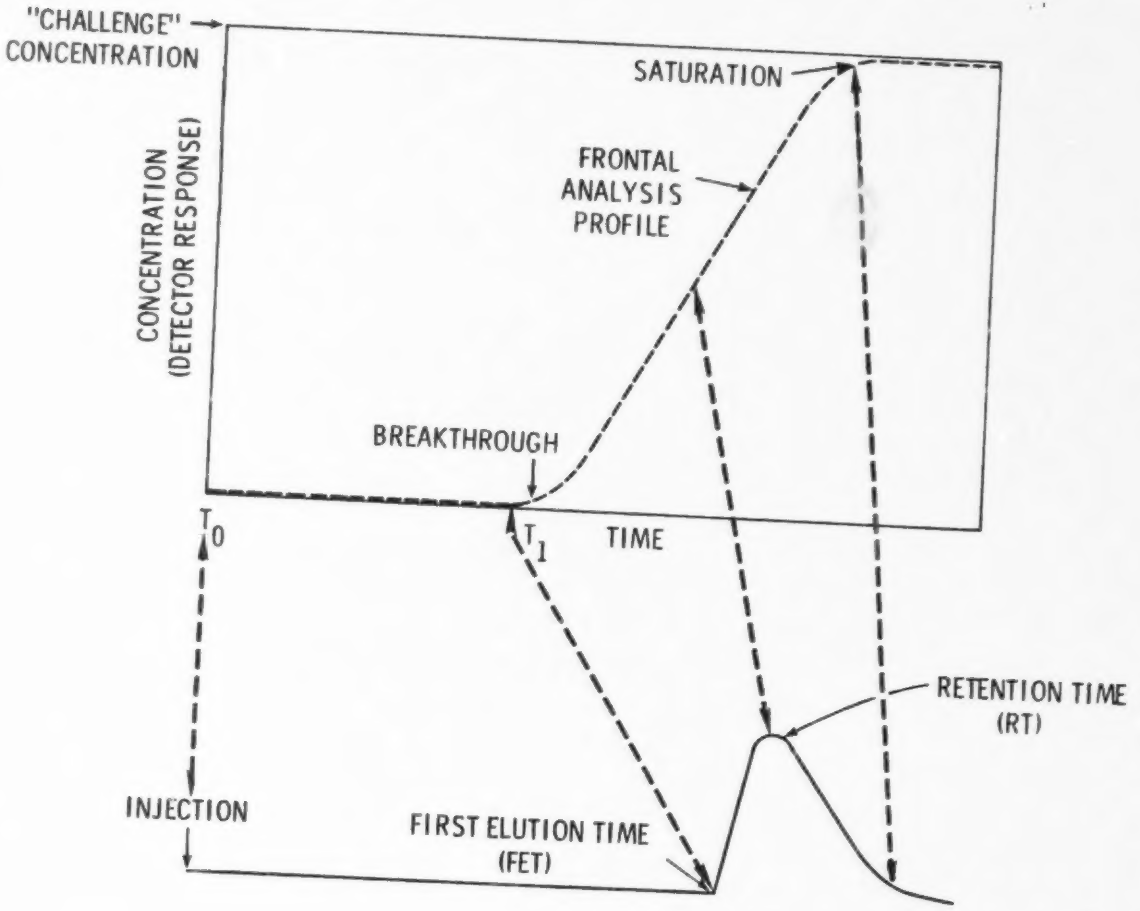

"CHALLENGE" CONCENTRATION
CONCENTRATION (DETECTOR RESPONSE)
SATURATION
FRONTAL ANALYSIS PROFILE
BREAKTHROUGH
T_0
T_1
TIME
RETENTION TIME (RT)
INJECTION
FIRST ELUTION TIME (FET)

Figure 24. Comparison of "frontal" and "elution" methods of sorbent capacity determination.

and acrylonitrile. These results are compiled in Table 19 and compared to their estimated values. Generally the "frontal analyses" showed the sorbent cartridges' capacities to be less than those estimated, though usually in the same order of magnitude (except for carbon tetrachloride). "Breakthrough" of the challenge compounds from the Ambersorb cartridges was very difficult to detect because slow "breakthrough" was indistinguishable from baseline drift. Based on these studies, the anticipated retention capabilities of the sorbent cartridges shown in Table 18 was judged to be plausibly realistic. The analyses of backup tubes during the collection of actual field samples was thought to be the best means of demonstrating the collection capabilities of the selected sorbent cartridges, since matrix effects could greatly alter sorbent capacities.

Desorption Properties--
After a sample has been collected and concentrated on a sorbent tube, two major techniques, thermal and solvent desorption exist for recovering the sample from the tube for analysis. In thermal desorption, a sorbent tube containing a sample is heated to a temperature high enough to volatilize the sample, such that a stream of carrier gas flowing through the sorbent will cause the sample to quickly migrate from the tube into an analytical system. The capillary inlet system, discussed previously, was designed for the thermal desorption of sorbent cartridges. With solvent desorption, the sample is recovered from the sorbent tube by extracting the sorbent with an appropriate solvent. The resulting solution is then introduced into an analytical system by syringe injection.

Thermal and solvent desorption have different advantages. For example, solvent desorption permits numerous replicate analyses, but the solvent dilutes the sample of interest (often >1000 fold). This defeats at least some of the sample concentration accomplished by sorbent sampling and reduces overall method sensitivity. On the other hand, thermal desorption can achieve a maximum sensitivity by introducing all of a collected sample into an analytical system; however, this does not permit replicate analyses. By splitting a thermally desorbed sample, replicate analyses can be performed but sensitivity is decreased by the amount of the split.

A brief study was conducted to compare thermal and solvent desorption. Two solvent desorption techniques, shown in Figures 25 and 26, were compared to thermal desorption of benzene from Ambersorb XE-340 cartridges. The benzene samples were generated with the Sample Generation System (Appendix B) and compared to analytical standards. A sample of benzene was also thermally desorbed from a Porapak R cartridge for comparison. The recoveries obtained, based on the theoretical amount of benzene generated, are given in Table 20. Assuming the actual amount of

TABLE 19. RESULTS OF FRONTAL ANALYSES OF SORBENT TUBES

			Sampling parameters			"Elution"	Frontal analyses information						
							Breakthrough			Saturation		Total exposure	
Compound	Sorbent	Weight, g	Rate, L/min	Temp., °C	Pressure, atm	capacity estimate @20°C	Time, min	Amount, µg	Volumetric capacity, L/g	Time, min	Amount, µg	Time, min	Amount, µg
Carbon tetrachloride	Tenax-GC	0.9	∿1.025	∿25	∿1	$>1.02 \times 10^4$[a]	<0.5	<3.6	<0.57	∿3	∿21	∿13	∿92
	Porapak R	1.5	∿0.886	∿25	∿1	$>6.6 \times 10^5$[a]	∿30	∿184	∿18	-[b]	-	∿51	∿313
	Ambersorb XE-340	3.2	∿0.975	∿25	∿1	$>4.0 \times 10^5$[c]	-[d]	-	-	-	-	∿420	∿2,840
Benzene	Tenax-GC	0.9	∿0.979	∿25	∿1	82[e]	∿8	∿30	∿8.7	-[b]	-	∿39	∿147
	Porapak R	1.5	-	-		175[e]	-[f]	-	-	-	-	0	0
	Ambersorb XE-340	3.2	-	-	-	$>4.0 \times 10^5$[g]	-[f]	-	-	-	-	0	0
Acrylonitrile	Tenax-GC	0.9	∿1	∿25	∿1	8.4[e]	2.5	8.5	∿3	>7.5	∿26	∿24	∿21
	Porapak R	1.5	∿1	∿25	∿1	25.2[e]	∿13	∿44	∿9	27.5	∿94	∿38	∿128
	Ambersorb XE-340	3.2	∿1	∿25	∿1	>24,000[h]	-[i]	-	>206	-	-	∿660	∿2,250

[a] Based on the fact that δ_m for carbon tetrachloride is greater than δ_m for benzyl chloride.

[b] Exposure discontinued before saturation obtained.

[c] Based on the fact that δ_m for carbon tetrachloride is greater than δ_m for n-hexane.

[d] Results were inconclusive.

[e] Previously determined.

[f] Not completed.

[g] Based on the fact that δ_m for benzene is greater than δ_m for n-hexane.

[h] Based on the fact that δ_m for acrylonitrile is greater than δ_m for n-pentane.

[i] Exposure discontinued before breakthrough obtained.

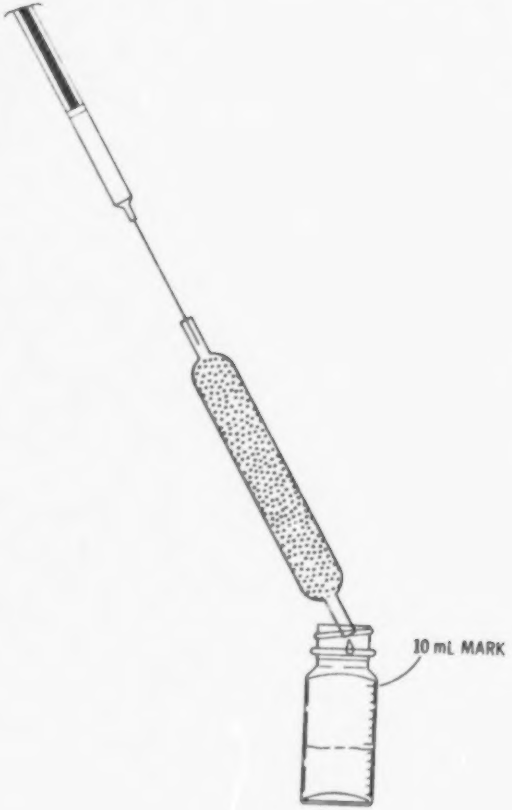
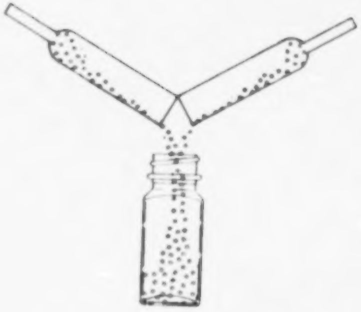


Figure 25. "Pass-through" solvent desorption technique.


A. EMPTY TUBE CONTENTS

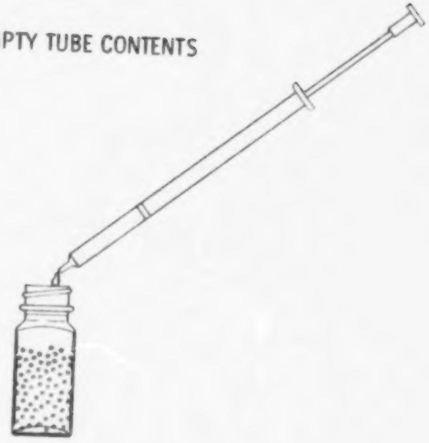

B. ADD SOLVENT

Figure 26. Solvent "bath" desorption technique.

TABLE 20. EVALUATION OF THE DESORPTION EFFICIENCY OF BENZENE FROM AMBERSORB XE-340

Sample	Theoretical amount, µg	Amount recovered, µg	Percent recovery
First wash of benzene exposed Ambersorb tube	0.90	0.76	84
Second wash of benzene exposed Ambersorb tube	$\sim$0	0.01	(1.2)[b]
Ambersorb tube emptied in acetone bath	0.90	0.59	66
Benzene exposed Porapak R tube thermally desorbed	$\sim$5.7[c]	7.9	138
Benzene exposed Ambersorb tube thermally desorbed	0.86	1.38	160

[a] The amount theoretically contained within the sample.

[b] The percentage of the first wash of that tube.

[c] Sampling rate and time were inaccurate, so that the actual amount of the sample may be higher than that indicated.

benzene generated was somewhat higher than the theoretical amount, more efficient recovery was indicated by thermal desorption. In another experiment, some laboratory air samples were collected with the sorbent cartridges and then analyzed. One Ambersorb XE-340 tube was solvent desorbed with little detected during its analysis. A similar Ambersorb XE-340 sample that was thermally desorbed yielded a much more complex chromatogram, demonstrating the superior sensitivity attainable by thermal desorption. Therefore, thermal desorption was selected as the most suitable sample recovery technique.

Two methods were used to determine the efficiency of recovering some of the twenty selected compounds from the sorbent cartridges by thermal desorption. One technique was to inject analytical standards through a septum see (Figure 14, Section 6) into a sorbent cartridge enclosed by the capillary inlet system desorption chamber. The sample was then desorbed through the entire sorbent cartridge into the analytical system. The recoveries summarized in Table 21 were obtained by comparing results of standards desorbed through sorbent cartridges to results of standards desorbed through an empty glass cartridge. The other method was to collect a vaporous compound mixture made with the Sample Generation System on sorbent cartridges and thermally desorb these cartridges. The results were quantitated by comparison to analytical standards

TABLE 21. RECOVERY OF STANDARDS FROM SORBENT TUBES

Compound	Sorbent material[a]		
	Tenax	Porapak R	Ambersorb
Carbon tetrachloride	79	101	10
Vinyl acetate	105	107	-[b]
Benzene	109	102	81
Tetrachloroethylene	110	91	51
Ethylene dichloride	108	104	15
1,4-Dioxane	105	100	-[b]
Ethylene dibromide	129	90	-[b]
Styrene	106	-[c]	-[c]
Hexachloro-1,3-butadiene	108	-[c]	-[c]
Benzyl chloride	59	-[c]	-[c]

[a] Values under sorbents are percentages found versus theoretical amounts.

[b] No peak of similar retention time observed.

[c] Not evaluated.

and these values compared to the theoretical amounts collected from the Sample Generation System. The recoveries obtained are compiled in Table 22. Assuming the actual concentrations of the generated compounds were somewhat different than their theoretical concentrations, certain recovered amounts were selected as representing true values. The recoveries obtained from various sorbent tubes could then be compared to each other as given in Table 23. These recovery experiments demonstrated that most of the compounds evaluated were efficiently desorbed from the Tenax and Porapak R sorbent cartridges; however, recoveries of compounds from Ambersorb XE-340 cartridges were biased in favor of the less polar compounds. If these sorbent cartridge are combined in series with the Ambersorb tube last, most high-molecular weight and polar compounds should be adsorbed on the Tenax and Porapak R tubes. Therefore, most compounds not efficiently desorbed from Ambersorb should be retained on the sorbent tubes prior to it.

As mentioned previously, the cartridge design given in Figure 22 was selected as potentially offering both acceptable thermal recoveries and an acceptable pressure drop, while containing sufficient sorbent to collect the compounds of interest (Table 18). Greatly increasing the diameter of the cartridge or the amount of sorbent in the cartridge would further decrease the ability to thermally desorb compounds from the sorbent cartridges. However, slightly increasing the diameter of the cartridges without increasing the amount of sorbent would probably decrease desorption efficiency only slightly, while the pressure drop across the tube would decrease significantly. Furthermore, solvent desorption

TABLE 22. PERCENT RECOVERIES OF THEORETICAL AMOUNTS OF GENERATED SAMPLES

		Compound[a]									
Tube #	Tube Type	Acrolein	Carbon tetra-chloride	Vinyl acetate	Ben-zene	Acrylo-nitrile	Tetra-chloro-ethylene	Dioxane	Ethylene di-chloride	Average % of theoretical amount	R.S.D. of theoretical percentages, %
18	Porapak R	20	84	81	126	47	47	42	180	78	67
67	Porapak R[b]	50	78	57	77	17	27	25	105	54	57
54	Ambersorb	11	17	18	143	52	23	20	124	51	103
119	Tenax-GC	41	212	72	66	38	69	39	78	77	74

[a] Values under compounds are the percentages found versus the theoretical amounts.

[b] Analyzed one week after tube #18.

TABLE 23. PERCENT RECOVERIES OF SELECTED AMOUNTS OF GENERATED SAMPLES

		Compound[a]									
Tube #	Tube Type	Acrolein	Carbon tetra-chloride	Vinyl acetate	Ben-zene	Acrylo-nitrile	Tetra-chloro-ethylene	Dioxane	Ethylene di-chloride	Average % of selected amount	R.S.D. of percentages, %
18	Porapak R	39	100[b]	100[b]	100[b]	100[b]	100[b]	100[b]	100[b]	92	23
67	Porapak R[c]	100[b]	93	71	61	37	58	60	58	67	30
54	Ambersorb	21	20	22	113	112	48	48	69	57	68
119	Tenax-GC	83	253	89	52	82	148	93	43	105	64

[a] Values under compounds are the percentages found versus the selected amounts.

[b] Selected amount -100% by definition.

[c] Analyzed one week after tube #18.

results in an unacceptable decrease in method sensitivity. Therefore, the cartridge design shown in Figure 22 was tentatively selected for use in the Portable Miniature Collection System. Slightly wider shorten tubes were to be considered if the pressure drop across this system (with cartridges as shown in Figure 22) were found to be too great for the DuPont P4000 personal pumps.

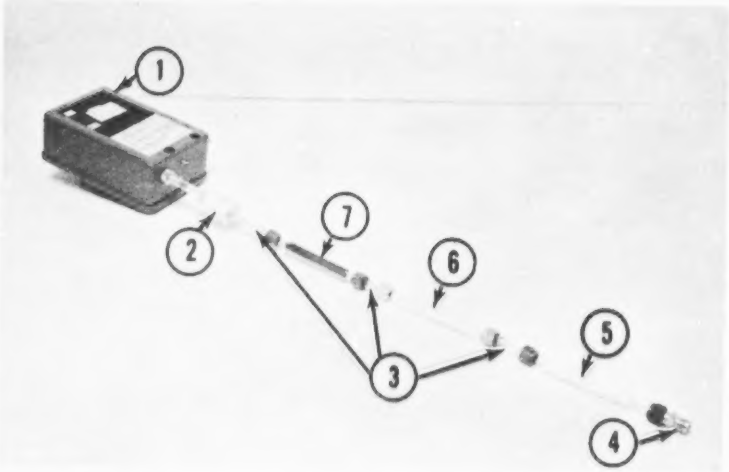
Sampling System

The ability of a pump to draw air through the selected sorbent cartridges in parallel and series modes was compared using a DuPont P4000 pump attached to "breadboarded" configurations of sampling systems in the two sampling modes. These configurations are shown in the photograph in Figure 27 and the schematic in Figure 28. A comparison of these two sampling configurations demonstrated that with the small personal pump a flow rate of ~1 L/min per tube could be attained with the series arrangement, while only ~0.5 L/ min per tube could be attained with the parallel arrangement. The reduced flow rate attained in the parallel configuration was attributed largely to the metering valves used to adjust the flows through the different sorbent cartridges. The valves, rotometers and other additional parts required for the parallel sampling arrangement would result in a sampling system with greater cost, weight, and complexity, and less accuracy, durability, and flow capability. Furthermore, the series configuration would have the additional advantage of fractionating compounds in air samples into zones of different volatilities on the different sorbent cartridges, thereby aiding the subsequent chromatographic separation of the complex samples. Therefore, the series arrangement was selected as the more suitable for the Portable Miniature Collection System.

For convenience, a tray was designed to contain the sorbent cartridges during sampling. The specifications of this sorbent tube tray and the procedure of "loading" it are given in the Operation Manual for the Portable Miniature Collection System (Appendix A). Figure 29 shows a "loaded" sorbent tube tray ready for sample collection.

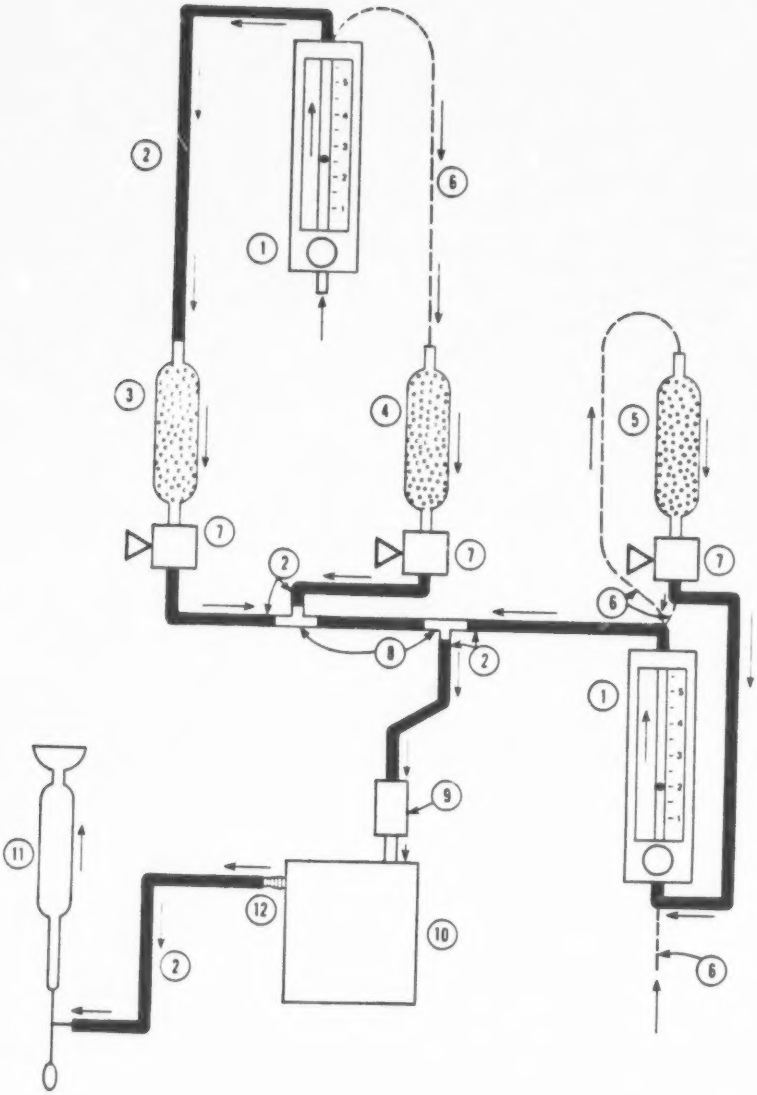
RESULTS

Based on laboratory evaluation, a portable, multi-residue sampling system was developed for the collection of ambient air samples. This system, shown in Figure 30, was designed to collect a broad variety of organic compounds from the atmosphere and should effectively collect and subsequently release the compounds of interest for this project. An Operation Manual, given in Appendix A, was written in draft form prior to field evaluation of this sampling system and finalized for this report. This manual describes the preparation, fabrication, operation, and maintenance of the Portable Miniature Collection System.



1 - DUPONT P4000 PUMP
2 - PUMP PRE-FILTER
3 - TYGON TUBING
4 - GLASS WOOL PLUG
(PARTICULATE FILTER)
5 - TENAX-GC CARTRIDGE
6 - PORAPAK R CARTRIDGE
7 - AMBERSORB XE-340
CARTRIDGE

Figure 27. "Breadboarded" version of the portable miniature sampling system with sorbent tubes in series.



1 - BROOKS 500 cc/min ROTAMETERS
2 - RUBBER TUBING
3 - TENAX-GC SORBENT TUBE
4 - PORAPAK R SORBENT TUBE
5 - AMBERSORB XE-340 SORBENT TUBE
6 - ALTERNATE POSITIONS FOR TUBING
7 - NEEDLE VALVES
8 - SWAGELOK TEES
9 - PUMP PRE-FILTER
10 - DUPONT P4000 PUMP
11 - BUBBLE METER
12 - EXHAUST BARB

Figure 28. Schematic of the "Breadboarded" version of the sampling system with the sorbent tubes in parallel.

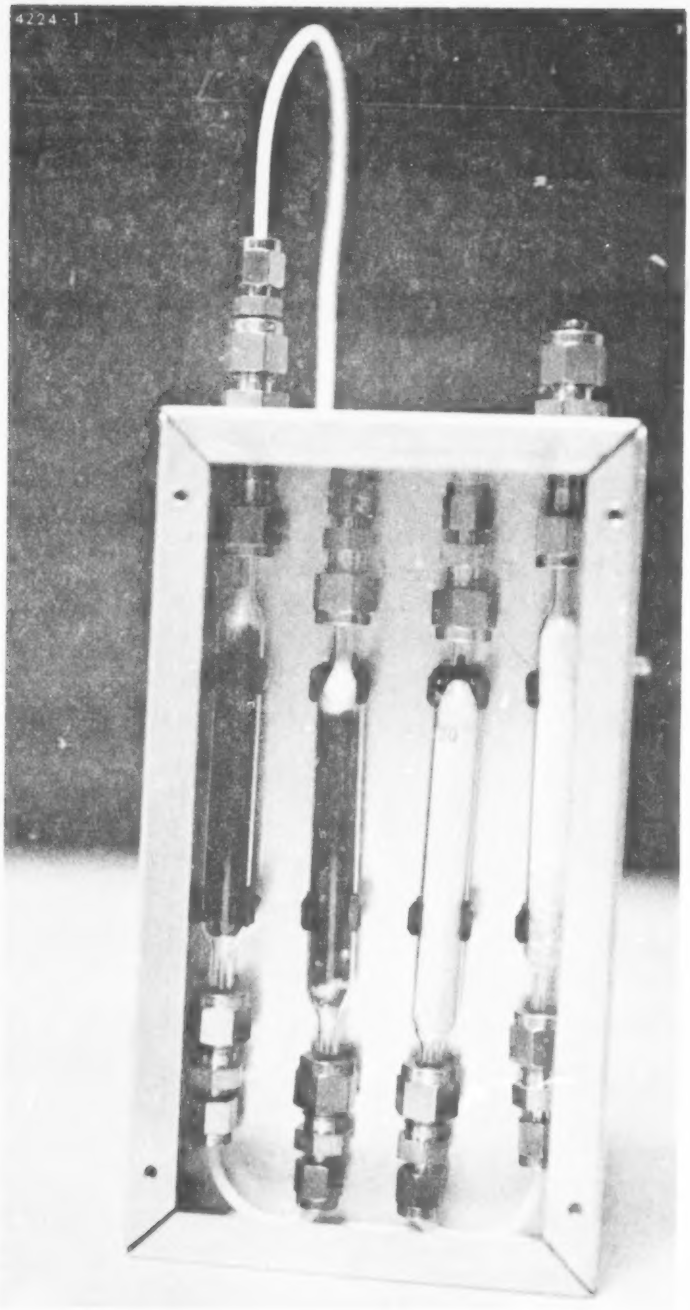


Figure 29. The "tube tray" portion of the Ambient Air Collection System.

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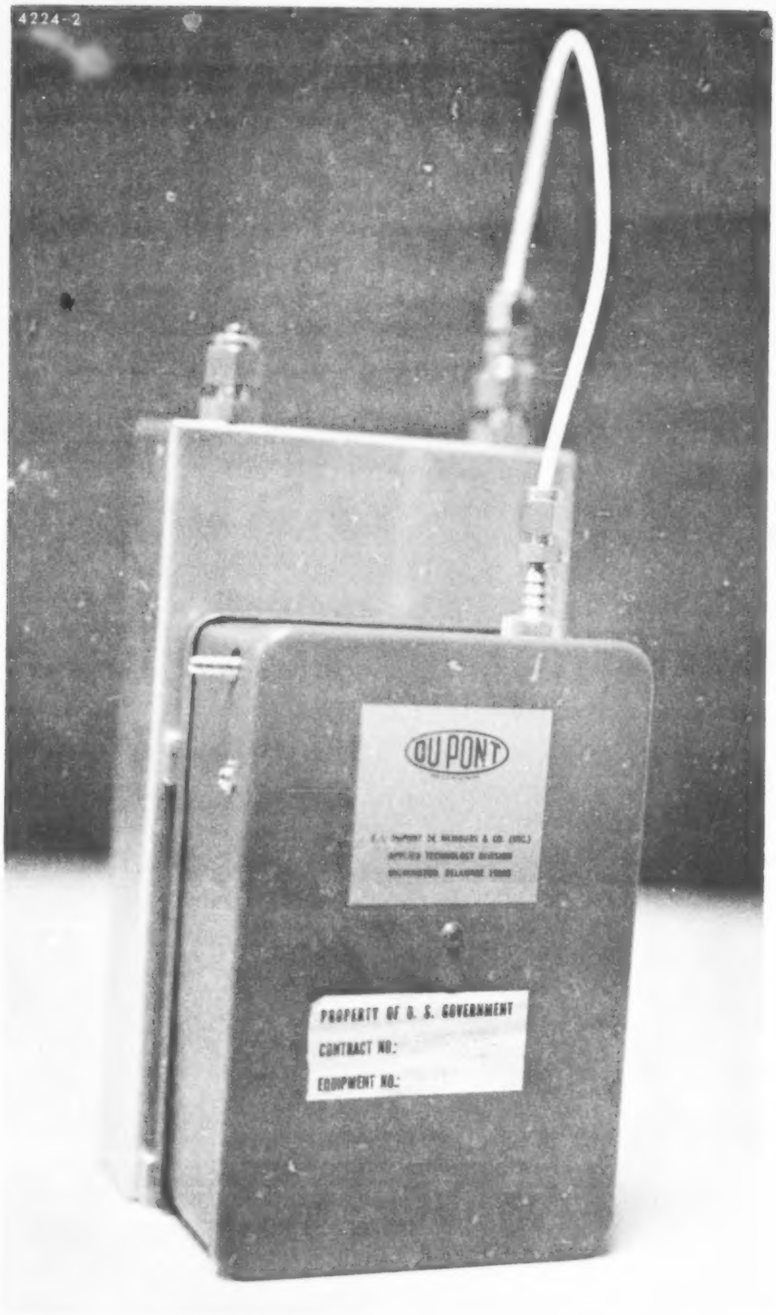
4224-2
DU PONT
E. I. DuPONT DE NEMOURS & CO. (INC.)
APPLIED TECHNOLOGY DIVISION
WILMINGTON, DELAWARE 19898
PROPERTY OF U. S. GOVERNMENT
CONTRACT NO:
EQUIPMENT NO:

Figure 30. Portable Miniature Collection System.

The collection of field samples with the Portable Miniature Collection System is discussed in Section 8. As this section reveals, mechanical problems were encountered with the DuPont P4000 pumps, especially with the drive belts slipping and breaking. Therefore, an attempt was made to improve the reliability of the Portable Miniature Collection System by modifying its design.

DISCUSSION

The Portable Miniature Collection System combines, in series, three commercially available solid sorbent materials, each within a discrete glass cartridge. These sorbents, Tenax-GC, Porapak R, and Ambersorb XE-340, have complimentary adsorption characteristics. When combined in series in an air sampling system, each sorbent retains a certain range of compounds for subsequent analysis. Figure 31 displays the theoretical performance of a multi-residue sampling system. An ambient air sample contains a wide variety of compounds including those of high, intermediate, and low volatility (represented by squares, triangles, and circles, respectively, in Figure 31). All of the compounds in the air sample are concentrated to varying degrees on the first sorbent tube (Tenax-GC). Low volatility compounds (squares) are concentrated quantitatively at the head of the first tube. Such compounds experienced very little chromatographic displacement down the sorbent tube because they partition more into the stationary (sorbent) than mobile (air) phase of the system. Very volatile compounds (circles), however, partition mostly into the mobile (air) phase and rapidly pass through the first tube. They frequently are not concentrated to analytically detectable levels. Compounds of intermediate volatility (triangles) may be concentrated to detectable levels, but also eventually pass through the first sorbent tube. Intermediate and high volatility compounds which elute from the first tube pass into a second sorbent tube (Porapak R) which has greater affinity for volatile organics. Again, all compounds are concentrated on the second tube to varying degrees. Compounds partitioning more into the stationary (sorbent) than mobile (air) phase are retained while very volatile compounds are concentrated but eventually pass through this second tube as well. The very volatile compounds which pass into the third sorbent tube (Ambersorb XE-340) are retained by this tube. The ability of the Portable Miniature Collection System to perform as theoretically described was evaluated with field samples. The results of these field evaluations are given in Sections 9.

In addition to the ability to collect atmospheric organics, the sorbent cartridges should also be able to release organics for analysis. As indicated previously, not all organics may be quantitatively released from the cartridges of the Ambient Air Collection System. In particular, very volatile, polar organics may be difficult to recover from the Ambersorb tubes. Consequently, field evaluations included a study of spiking techniques (see Sections 8 and 9).

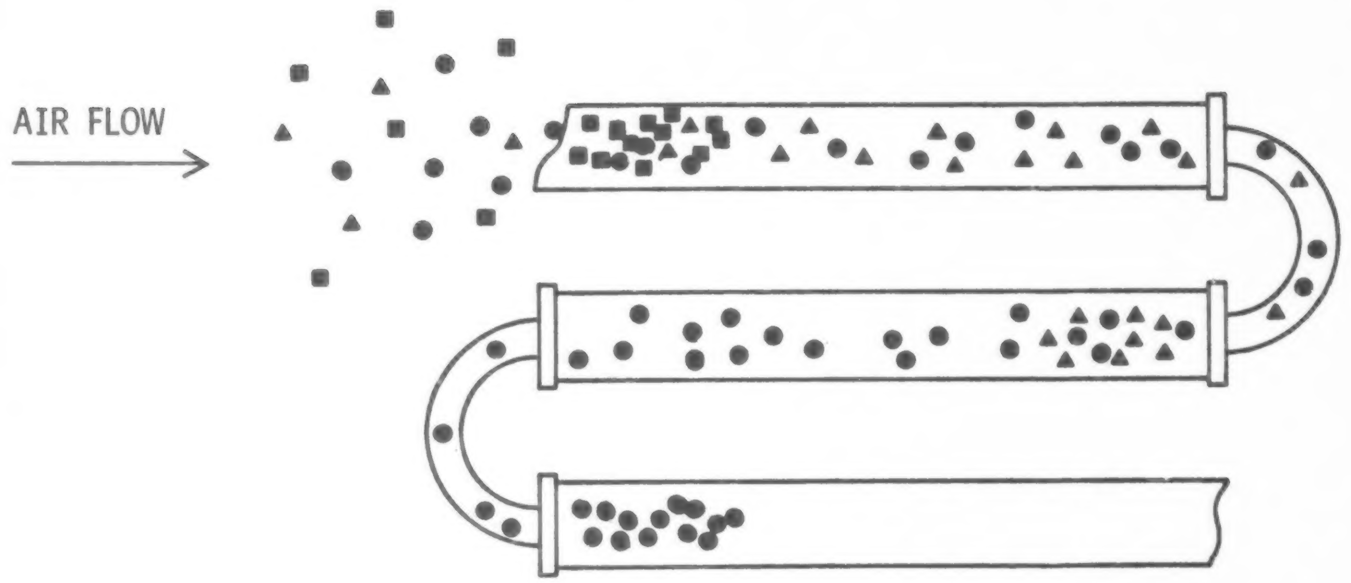

Figure 31. Theoretical performance of multi-residue sampling system.

SECTION 8

COLLECTION OF FIELD SAMPLES

OBJECTIVE

The purpose of the field sampling phase of this program was to test the newly developed sampling and analytical methodology under actual field conditions. This included evaluation of the difficulty of transporting the sampling system and accessories, of operating this system in the field, and, later, of analyzing complex environmental samples. The analyses of these samples are discussed in Section 9.

INSTRUMENTATION

The Portable Miniature Collection System which was developed for this project (see Section 7), was used to collect field samples. The Operation Manual for this system, given in Appendix A, describes the preparatory and sampling procedures for using this system, as well as the details of its fabrication. Although the operation manual was drafted prior to field sampling, experience gained during this work was used to modify the procedures in the original draft. These modifications are included in the final version of the manual presented in this report. Most of the modifications were relatively minor, such as wrapping sorbent tubes with glass wool to minimize breakage of sorbent and culture tubes. Three-exceptions were the development of a mechanical leak check procedure (included in Appendix A), the modification of sorbent tube design and the change of type of personal pump. These alternations were the result of field sampling experience. The leak-check procedure was first instituted during the collection of samples in Houston, Texas. The Spectrex pumps were used at Research Triangle Park, North Carolina and Cincinnati, Ohio with sorbent tubes all of the modified design (wider diameter-15 mm O. D.).

FIELD SAMPLING

Dayton

Samples were first collected at Carillon Park in Dayton, Ohio. They were obtained with the use of the Portable Miniature Collection Systems using DuPont personal pumps and sorbent tubes with the narrower design (12 mm O.D.). The sampling plan used is given in Table 24, while Table 25 provides the actual sampling conditions. No problems were experienced with either system during this sampling experiment.

Since the Carillon Park is very near Monsanto Research Corporation, equipment and personnel were driven to the park. The equipment was loosely carried in boxes without packing materials, but since the drive was short, no breakage problems were encountered. Samples were collected on 3 April 1980 on the stairs of the Bell Tower at Carillon Park. The day was sunny and mild [~15°C(~60°F)] with a slight breeze and a modest haze.

Los Angeles

The sampling plan developed for the collection of samples in Los Angeles is given in Table 26. In addition to those samples shown, samples were also collected with an Ambient Air Collection System (developed for EPA Contract 68-02-2773) during the same time periods. Although total sample volumes collected by the Portable and Ambient Air Systems were different, the samples could be considered replicates. Extra, blank sorbent tubes were also taken on that sampling trip to replace any sorbent tubes broken during shipment. Spiking solutions are described in Tables 27 through 31.

Sampling personnel and all equipment were flown from Dayton to Los Angeles, with the equipment sent as baggage. The equipment was carefully packed in sturdy containers with plenty of cushioning packing material. Sorbent tubes were wrapped with glass wool inside the culture tubes to minimize breakage. No problems were encountered in shipment other than to assure airline officials that the materials inside were not hazardous and were securely packaged. No damage to equipment occurred on either the out-going or return flights, except the breakage of a few culture tubes.

The sampling site was on the roof top of the Education Resource Center Building located on the grounds of the California State University, Dominguez Hills campus. A map of the Los Angeles area, provided in Figure 32, shows the campus slightly north of area A. Areas A, B, and C correspond to locations estimated to be high in concentrations of the compounds of interest by computer Climatological Dispersion Modeling. Data for this model were obtained from the MRC Source Assessment Data Base which incorporates stack emission data from numerous sources. Table 32 gives the computer estimated composition of air pollution in these areas for some of the compounds of interest and a few others.

The samples were collected on 14 and 15 April 1980. On 14 April 1980 the temperature in Los Angeles ranged from approximately 18°C to 27°C (65°F to 80°F), the relative humidity from about

TABLE 24. SAMPLING PLAN - DAYTON

Sample number	Sorbent	Purpose	Tray position	Sampling				Pump information	Other information
				Date	Times	Volume	Flow rate		
1	Tenax	Sample	1	4-3-80	~0800 -1600 hr	~480 L	~1 L/min	Portable System	
	Porapak R	Sample	2						
	Ambersorb	Sample	3						
	Ambersorb	Backup	4						
C	Tenax	Calibration	1	4-3-80					Calibration of sampling system flow rates.
	Porapak R	Calibration	2						
	Ambersorb	Calibration	3						
	Ambersorb	Calibration	4						
2	Tenax	Sample	1	4-3-80	~1200 -1600 hr	~240 L	~1 L/min	Portable System	
	Porapak R	Sample	2						
	Ambersorb	Sample	3						
	Ambersorb	Backup	4						
B	Tenax	Blank							Blanks
	Porapak R	Blank							
	Ambersorb	Blank							

TABLE 25. SAMPLING CONDITIONS - DAYTON

Sample number	Date	Times	Flow rate, L/min	Volume estimated from flow rate, L	Comments
1	4-3-80	1128-1558 hr	~0.8	~220	No pump problems.
2	4-3-80	0810-1610 hr	~0.6	~290	No pump problems.

25% to 49%, and the winds from the northwest to west-southwest. On the following day, 15 April 1980, weather conditions were similar: the temperature range was approximately the same; the relative humidity slightly less and more stable (around 32%); and the winds more gusty, mainly from the northwest. Several exhaust stacks could be seen from the sampling location to the north, northwest, and southwest of the Dominguez Hills campus.

Table 33 describes the sampling conditions. Problems were experienced with the DuPont pumps of the Portable Miniature Collection Systems. Pump #2 drew air in an irregular fashion both sampling periods, necessitating a flow decrease during the first period. The drive belt of Pump #1 came off during the second sampling period.

Niagara Falls

The ability of the Portable Miniature Collection Systems to sample unattended was tested during an indoor sampling trip in Niagara Falls. The sampling plan is given in Table 34. As indicated, three, consecutive, twelve-hour samples were to be taken with the system unattended during the majority of the sampling periods. Samples were collected in a private residence with temperatures ranging from 24°C to 27°C (75° to 81°F). As indicated in Table 35, this system did not function well under these strenuous circumstances with discontinuous operation during the first and second sampling periods. Pump #1 did not operate at all during the third sampling period. After returning to the laboratory, the DuPont pump had to be completely overhauled (replacing valves and diaphragms) in order to be restored to operating conditions.

Houston

The sampling plan developed for the collection of Houston air samples is given in Table 36. In addition to those samples shown, samples were also collected with the Ambient Air Collection System and a critical orifice system developed for another project.

TABLE 26. SAMPLING PLAN - LOS ANGELES

Sample number	Sorbent	Purpose	Tray position	Sampling Date	Sampling Times	Sampling Volume	Sampling Flow rate	Pump information	Other information
1	Tenax	Sample	1	4-14-80	~0800 -1600 hr	~480 L	~1 L/min	Portable System, DuPont Pump #1	
	Porapak R	Sample	2						
	Ambersorb	Sample	3						
	Ambersorb	Backup	4						
2	Tenax	Sample	1	4-14-80	~0800 -1600 hr	~480 L	~1 L/min	Portable System, DuPont Pump #2	
	Porapak R	Sample	2						
	Ambersorb	Sample	3						
	Ambersorb	Backup	4						
C	Tenax	Calibration	1	4-14-80 and 4-15-80					Calibration of sampling system flow rates.
	Porapak R	Calibration	2						
	Ambersorb	Calibration	3						
	Ambersorb	Calibration	4						
3	Tenax	Sample	1	4-15-80	~0800 -1600 hr	~480 L	~1 L/min	Portable System, DuPont Pump #1	
	Porapak R	Sample	2						
	Ambersorb	Sample	3						
	Ambersorb	Backup	4						
2	Tenax	Sample	1	4-15-80	~0800 -1600 hr	~1,000 L	~2-3 L/min	Portable System, DuPont Pump #2	Field spike - see Method A
	Porapak R	Sample	2						
	Ambersorb	Sample	3						
	Ambersorb	Backup	4						
B	Tenax	Blank							Blanks
	Porapak R	Blank							
	Ambersorb	Blank							
FS	Tenax	Spike							Transport spikes - see Method B
	Porapak R	Spike							
	Ambersorb	Spike							
LS	Tenax	Spike							Lab spikes - see Method B
	Porapak R	Spike							
	Ambersorb	Spike							

Spiking Method A - ~5 min after starting sample collection, inject 1 μL quantities each of spiking solutions A, C, and E (see Tables 27, 29, and 30) into the glass wool plug of the system inlet.

Spiking Method B - Inject 1 μL quantities of each spiking solution ~3 mm (1/8 in.) into the sorbent beds of the tubes below at their unnumbered ends.

Tenax - C, E, F (see Tables 26 to 31)
Porapak R - A, B, C
Ambersorb - A

TABLE 27. FIELD SPIKING SOLUTION A

Compound	Concentration, µg/mL
Acrolein	93
Carbon tetrachloride	120
Vinyl acetate	132
Benzene	76
Acrylonitrile	81
Ethylene dichloride	56
1,4-Dioxane	133
Tetrachloroethylene	59
Ethylene dibromide	202
Acetone[a]	

[a] Solvent.

TABLE 28. FIELD SPIKING SOLUTION B

Compound	Concentration, µg/mL
Tetrachloroethylene	55
cis-1,3-Dichloropropane	77
trans-1,3-Dichloropropene	76
Hexachloro-1,3-butadiene	163
Acetone[a]	

[a] Solvent.

TABLE 29. FIELD SPIKING SOLUTION C

Compound	Concentration, µg/mL
Styrene	92
Hexachloro-1,3-butadiene	191
Benzyl chloride	98
Acetone[a]	

[a] Solvent.

TABLE 30. FIELD SPIKING SOLUTION E

Compound	Concentration, μg/mL
Ethylene glycol	151
Di-(2-ethylhexyl) phthalate	42
Pentachlorophenol	68
Acetone[a]	

[a] Solvent.

TABLE 31. FIELD SPIKING SOLUTION F

Compound	Concentration, μg/mL
Benzidine	73
Chrysene	24
Benzo(a)pyrene	47
Toluene[a]	

[a] Solvent.

TABLE 32. LOS ANGELES - POTENTIAL CARCINOGENIC COMPOSITION AT POINTS OF MAXIMUM CONCENTRATION (micrograms per cubic meter)

Compound	Location A 86, 46	Location B 80, 46	Location C 82, 46
Acrylonitrile	0.0007	0.0030	0.0016
Benzene	0.01	0.01	0.01
Carbon tetrachloride	44	5	9
Chloroform	22	2	4
DDT	0.38	24.7	1.4
Ethyl Chloride	6	5	6
Ethylene dichloride	191	22	42
Vinyl chloride	117	12	23
Vinylidene chloride	0.16	0.05	0.02

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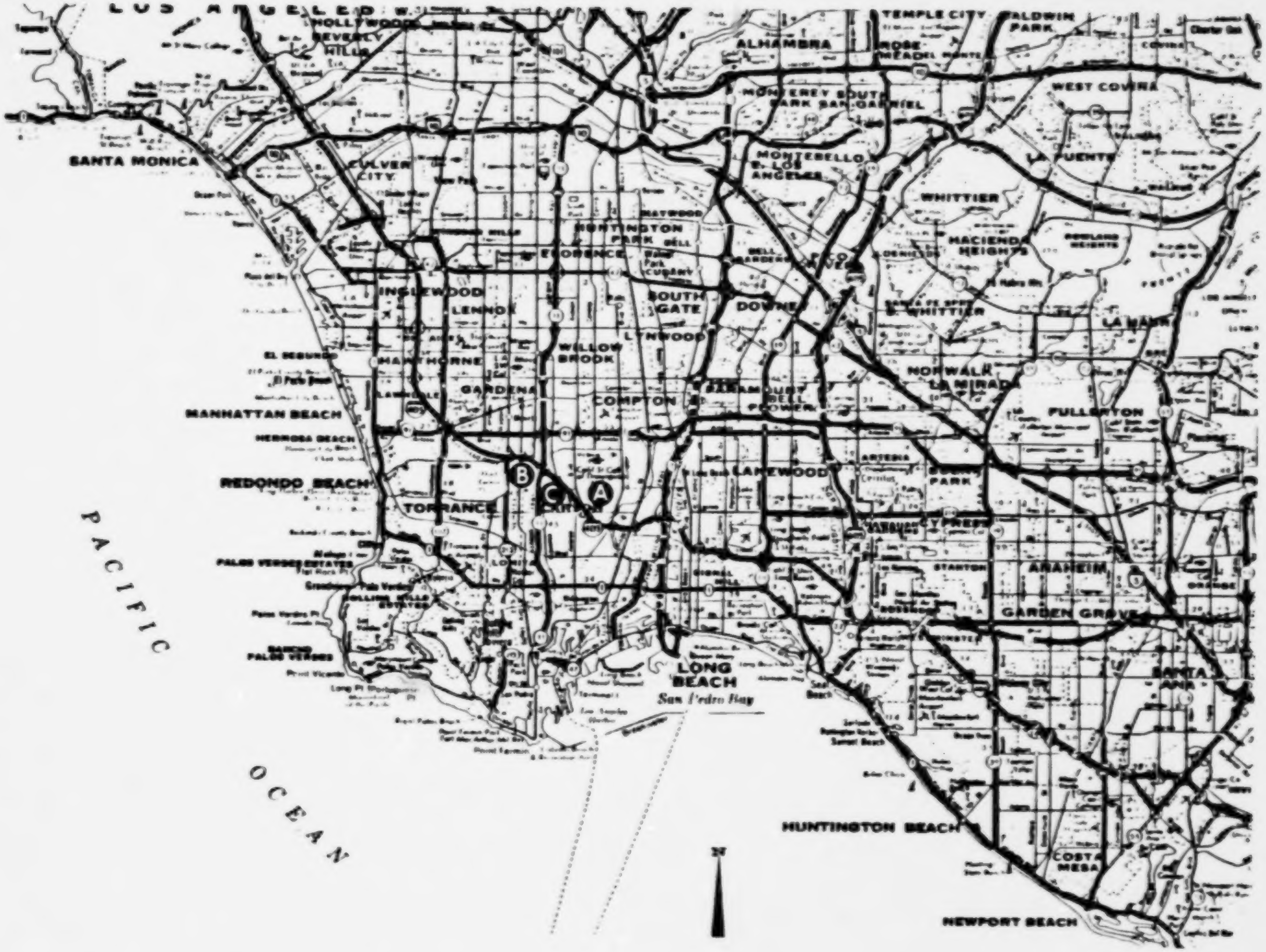
LOS ANGELES
HOLLYWOOD
BEVERLY HILLS
SANTA MONICA
CULVER CITY
ALHAMBRA
TEMPLE CITY
BALDWIN PARK
ROSEMEAD
WEST COVINA
MONTEREY PARK
SOUTH SAN GABRIEL
MONTEBELLO
E. LOS ANGELES
WHITTIER
LA PUENTE
HACIENDA HEIGHTS
HUNTINGTON PARK
BELL
FLORENCE
SOUTH GATE
DOWNEY
INGLEWOOD
LENNOX
LYNWOOD
HAWTHORNE
WILLOWBROOK
NORWALK
LA MIRADA
LA HABRA
GARDENA
COMPTON
PARAMOUNT
BELLFLOWER
FULLERTON
EL SEGUNDO
MANHATTAN BEACH
HERMOSA BEACH
REDONDO BEACH
TORRANCE
LAKEWOOD
BUENA PARK
CYPRESS
ANAHEIM
STANTON
GARDEN GROVE
PALOS VERDES ESTATES
ROLLING HILLS ESTATES
RANCHO PALOS VERDES
LONG BEACH
San Pedro Bay
SANTA ANA
HUNTINGTON BEACH
COSTA MESA
NEWPORT BEACH
A
B
C
N
PACIFIC
OCEAN

Figure 32. Locations of high ground level concentrations - Los Angeles, California.

TABLE 33. SAMPLING CONDITIONS - LOS ANGELES

Sample number	Date	Times	Flow rate, L/min	Volume estimated from flow rate, L	Comments
1	4-14-80	1004-1804 hr	~1.0	~470	No pump problems.
2	4-14-80	1026-1826 hr	~0.7	~350	Pump performance irregular; Flow reduced during sampling.
3	4-15-80	0840-1640 hr	~1.0	~480	Drive belt slipped off pump during last 2 hrs of sampling.
4	4-15-80	0859-1659 hr	~0.5	~250	Pump performance irregular. Spiked as directed.

Although total sample volumes collected by these three different systems were not identical, the samples were essentially replicates. Extra, blank sorbent tubes were taken to replace broken tubes and tubes spiked with the Sample Generation System were taken to provide transport and field spikes.

As with Los Angeles, personnel and equipment were flown to Houston. This time, airline officials were especially concerned that the materials and/or equipment might be hazardous. They were assured there was absolutely no hazard. Although the sorbent tubes were wrapped with glass wool inside the culture tubes, at least a dozen culture tubes broke during shipment. This damage was attributed to the soft-sided case in which they were packed. A sturdy case lined with cushioning materials would have been preferable.

The sampling was performed on the second floor balcony of a motel located 0.4 Km (1/4 mile) north of Route 225 on South Richie Road. This site was within area number 3 on the map shown in Figure 33. As with Figure 32, the locations marked on this map are areas estimated to have high levels of the pollutants of interest. This information was obtained by computer Climatological Dispersion Modeling with data from the MRC Source Assessment Data Base [1]. The estimated composition of some of the selected compounds and a few others in these areas are given in Table 37. The terrain surrounding the sampling area selected was relatively flat and oil refineries could be seen approximately 1.6 Km (1 mile) away in all directions.

TABLE 34. SAMPLING PLAN - NIAGARA FALLS

Sample number	Sorbent	Purpose	Tray position	Sampling				Pump information	Other information
				Date	Times	Volume	Flow rate		
1	Tenax	Sample	1	6-18-80	~0800-2000 hr	~720 L	~1 L/min		
	Porapak R	Sample	2						
	Ambersorb	Sample	3						
	Ambersorb	Backup	4						
2	Tenax	Sample	1	6-18-80	~0800-2000 hr	~720 L	~1 L/min	Portable System Pump #2	
	Porapak R	Sample	2						
	Ambersorb	Sample	3						
	Ambersorb	Backup	4						
3	Tenax	Sample	1	6-18-80 to 6-19-80	~2100-0900 hr	~360 L	~0.5 L/min	Portable System Pump #1	
	Porapak R	Sample	2						
	Ambersorb	Sample	3						
	Ambersorb	Backup	4						
4	Tenax	Sample	1	6-18-80 to 6-19-80	~2100-0900 hr	~360 L	~0.5 L/min	Portable System Pump #2	
	Porapak R	Sample	2						
	Ambersorb	Sample	3						
	Ambersorb	Backup	4						
5	Tenax	Sample	1	6-19-80	~1000-2200 hr	~500 L	~0.7 L/min	Portable System Pump #1	
	Porapak R	Sample	2						
	Ambersorb	Sample	3						
	Ambersorb	Backup	4						
6	Tenax	Sample	1	6-19-80	~1000-2200 hr	~500 L	~0.7 L/min	Portable System Pump #2	
	Porapak R	Sample	2						
	Ambersorb	Sample	3						
	Ambersorb	Backup	4						
B	Tenax	Blank							Blanks.
	Porapak R	Blank							
	Ambersorb	Blank							
C	Tenax	Calibration	1	6-18-80 and 6-19-80					Calibration of sampling system flow rates.
	Porapak R	Calibration	2						
	Ambersorb	Calibration	3						
	Ambersorb	Calibration	4						

TABLE 35. SAMPLING CONDITIONS - NIAGARA FALLS

Sample number	Date	Times	Flow rate, L/min	Volume estimated from flow rate, L	Comments
1	6-18-80				Not collected.
2	6-18-80	0808-2008 hr	~0.5	~290	Pump stopped after ~10 hrs.
3	6-18-80 to 6-19-80	2100-? hr	~0.5	?	Drive belt came off pump at unknown time.
4	6-18-80 6-19-80				Not collected.
5	6-19-80	1019-2157 hr	~0.4	~260	Pump not functioning. A Bendix pump substituted.
6	6-19-80				Not collected.

The samples were collected on 29 and 30 July 1980. Weather conditions were hot and humid both days, with temperatures exceeding 32°C (90°F) and relative humidity at approximately 90%. The sampling conditions are provided in Table 38. As mentioned previously, the leak check procedure specified in the Operation Manual was instituted during this sampling program.

Research Triangle Park

The portable miniature collection system was tested in Research Triangle Park, North Carolina October 29-31, 1980 to gather information on background levels of the ten organic compounds listed in Table 39. The system was worn by an EPA employee during a normal 24-hour period such that all of his normal environment (both home and office) was evaluated. The pertinent sampling data are included in Table 40. Outside temperatures varied in the 5-15°C (40-60°F) range during the sampling period and the general conditions were damp and rainy (relative humidities of 85-95%). The indoor temperatures were 18°C (65°F) in the home and 27°C (80°F) at the office.

Transportation of the tubes to and from the sampling site was accomplished as previously described with minimal breakage. This was the first time that the Spectrex Model PAS 3000 pump was used. Problems encountered during this sampling trip included inability to attain maximum charge on the portable battery packs due to

TABLE 36. SAMPLING PLAN - HOUSTON

Sample number	Sorbent	Purpose	Tray position	Sampling				Pump information	Other information
				Date	Times	Volume	Flow rate		
1	Tenax	Sample	1	7-29-80	~0800-1600 hr	~290 L	~0.6 L/min	Portable System Pump #1	
	Porapak R	Sample	2						
	Ambersorb	Sample	3						
	Ambersorb	Backup	4						
2	Tenax	Sample	1	7-29-80	~0800-1600 hr	~290 L	~0.6 L/min	Portable System Pump #2	
	Porapak R	Sample	2						
	Ambersorb	Sample	3						
	Ambersorb	Backup	4						
3	Tenax	Sample	1	7-29-80	~0800-1600 hr	~290 L	~0.6 L/min	Portable System Pump #3	Tenax tube spiked as below.
	Porapak R	Sample	2						
	Ambersorb	Sample	3						
	Ambersorb	Backup	4						
4	Tenax	Sample	1	7-29-80	~0800-1600 hr	~290 L	~0.6 L/min	Portable System Pump #4	
	Porapak R	Sample	2						
	Ambersorb	Sample	3						
	Ambersorb	Backup	4						
5	Tenax	Sample	1	7-30-80	~0800-1600 hr	~290 L	~0.6 L/min	Portable System Pump #1	Tenax tube spiked as below.
	Porapak R	Sample	2						
	Ambersorb	Sample	3						
	Ambersorb	Backup	4						
6	Tenax	Sample	1	7-30-80	~0800-1600 hr	~290 L	~0.6 L/min	Portable System Pump #2	
	Porapak R	Sample	2						
	Ambersorb	Sample	3						
	Ambersorb	Backup	4						
7	Tenax	Sample	1	7-30-80	~0800-1600 hr	~290 L	~0.6 L/min	Portable System Pump #3	
	Porapak R	Sample	2						
	Ambersorb	Sample	3						
	Ambersorb	Backup	4						
8	Tenax	Sample	1	7-30-80	~0800-1600 hr	~290 L	~0.6 L/min	Portable System Pump #4	
	Porapak R	Sample	2						
	Ambersorb	Sample	3						
	Ambersorb	Backup	4						
B	Tenax	Blank							Blanks.
	Tenax	Blank							
	Porapak R	Blank							
	Porapak R	Blank							
	Ambersorb	Blank							
	Ambersorb	Blank							
S	Tenax	Spike							Spikes - spiked with ~5 μg each of benzene, benzyl chloride, carbon tetrachloride, tetrachloroethylene, ethylene dibromide, cis-1,3-dichloropropene, and hexachloro-1,3-butadiene on Sample Generation System (Appendix A).
	Tenax	Spike							
	Porapak R	Spike							
	Porapak R	Spike							
	Ambersorb	Spike							
	Ambersorb	Spike							
C	Tenax	Calibration	1	7-29-80 and 7-30-80					Calibration of sampling system flow rates.
	Porapak R	Calibration	2						
	Ambersorb	Calibration	3						
	Ambersorb	Calibration	4						

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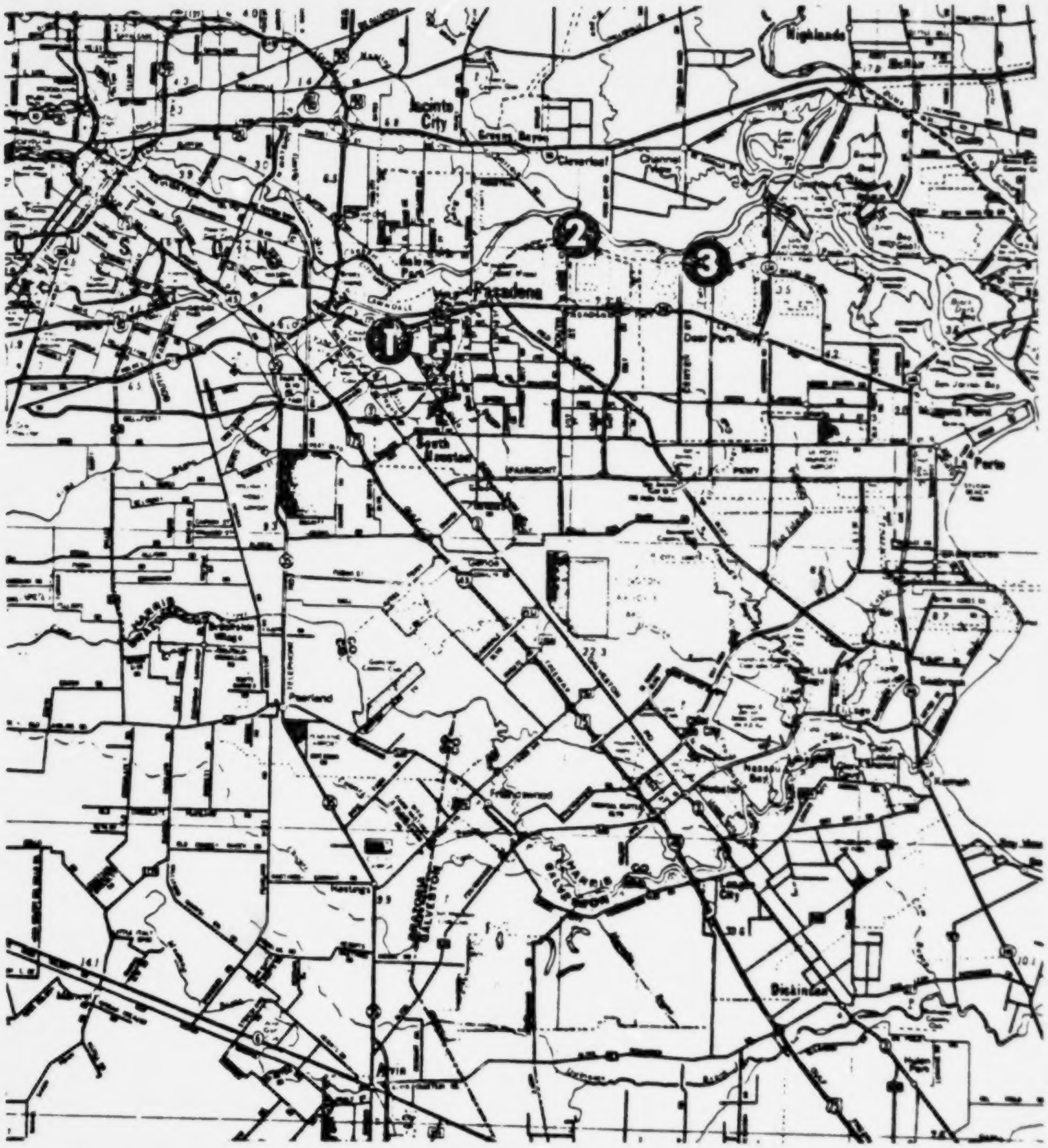
Highlands
Jacinto City
HOUSTON
2
3
Pasadena
1
Deer Park
South Houston
Pearland
Dickinson
Alvin

Figure 33. Locations of maximum concentration of pollutants in Houston.

TABLE 37. AVERAGE CONCENTRATIONS AT POINTS OF MAXIMUM POLLUTION IN HOUSTON (Micrograms per cubic meter)

Compound	Location 1 82,88	Location 2 90,92	Location 3 95,90
Acrylonitrile	1.0	0.1	0.1
Benzene	1,366.0	6.0	5.0
Carbon tetrachloride	6.0	190.0	251.0
Chloroform	2.0	92.0	123.0
Dichlorobutene	1.0	0.02	0.02
Ethylene dichloride	26.0	977.0	757.0
Tetrachloroethane	0.009	0.022	0.018
Epichlorohydrin	0.15	1.0	1.0
Trichloroethylene	5.0	12.0	10.0
Vinyl chloride	7.0	15.0	2.0
Vinylidene chloride	0.004	0.165	0.220
Ethylene dibromide	0.14	0.01	0.10

problems with scheduling of the sampling. Also the noise level of the pump was such that the wearer was unable to keep it in the room with him during sleeping hours, and it was consequently placed in an adjoining room. On one occasion a DuPont Model P4000 pump was used instead of the Spectrex. The drive belt broke sometime during the sampling period, invalidating that sample.

Cincinnati

A one-day sampling experiment was conducted on a trip from MRC (Dayton Laboratory) to the Environmental Protection Agency Offices in Cincinnati, Ohio. The portable miniature collection system (with Spectrex Model PAS3000 pump) was worn by an MRC employee to assess the concentrations of the target compounds that were previously measured at RTP. Temperatures during sampling were 21-22°C (70-72°F) with a relative humidity of ~40%. The system operated normally during a 7 hour and 55 minute sampling period at which time the low flow beeper sounded. Sampling was continued for an additional 10 minutes before terminating. The average flow rate over this period was 722 mL/min. A total sample volume of 350 L was collected.

TABLE 38. SAMPLING CONDITIONS - HOUSTON

Sample number	Date	Times	Flow rate, L/min	Volume estimated from flow rate, L	Comments
1	7-29-80	1141-1940 hr	~0.8	~370	Drive belt broken and replaced during sampling.
2	7-29-80	1113-1917 hr	~0.8	~360	Drive belt broken and replaced during sampling.
3	7-29-80				Not collected.
4	7-29-80				Not collected.
5	7-30-80	0830-1645 hr	~0.6	~300	Pump #1 ceased functioning and was replaced by Pump #3.
6	7-30-80	0800-1600	~0.6	~300	No problems.
7	7-30-80				Not collected.
8	7-30-80	0812-1612	~0.7	~310	No problems.

TABLE 39. RTP AND CINCINNATI TARGET COMPOUNDS

Chloroform
1,1,1-Trichloroethane
Benzene
Carbon tetrachloride
1,2-Dichloroethane
Trichloroethylene
Bromodichloromethane
Tetrachloroethylene
Chlorobenzene
1,1,2-Trichloroethane

TABLE 40. RTI SAMPLING DATA

Tube number	Sorbent	Date	Time	Volume sampled
509	Tenax	10/29	1830-2214	224L
505	Porapak-R			
454	Ambersorb			
539	Ambersorb			
455	Tenax	10/29-30	2215-0645	490L
514	Porapak-R			
473	Ambersorb			
540	Ambersorb			
545	Tenax	10/30	0730-1540	485L
528	Porapak-R			
441	Ambersorb			
537	Ambersorb			
470	Tenax	10/30	1835-2215	240L
459	Porapak-R			
523	Ambersorb			
450	Ambersorb			
549	Tenax	10/30-31	2233-0645	-[a]
456	Porapak-R			
474	Ambersorb			
426	Ambersorb			
501	Tenax	10/31	0712-1440	445L
492	Porapak-R			
500	Ambersorb			
486	Ambersorb			

[a] Pump belt broke during sampling run - no accurate volume obtained.

SECTION 9

ANALYSIS OF FIELD SAMPLES BY CAPILLARY GAS CHROMATOGRAPHY/ MASS SPECTROMETRY

OBJECTIVE

Samples of ambient air which were collected in the field with the Portable Sampling System were to be analyzed by capillary gas chromatography/mass spectrometry [$(GC)^2/MS$]. The analytical method, described in Section 6, for $(GC)^2$ analyses was adapted to a $(GC)^2/MS$ instrument for the evaluation of the field samples. The presence of the twenty selected potential carcinogens was investigated by reviewing mass spectral data. Compounds of interest identified in the field samples were then quantitated.

INSTRUMENTATION

A Hewlett-Packard Model 5985 GC/MS system was used for the analysis of field samples. This instrument had a Model 5840 GC with a capillary inlet system which was very similar to the GC used during the analytical method development phase of this program (Section 6). A data system, that was also part of this instrument, was used to display, interpret, and reduce mass spectral data. Final interpretation of mass spectral data was performed by a qualified mass spectroscopist.

To introduce samples from sorbent tubes into this analytical system, the capillary inlet system (Section 6) was interfaced to the Model 5985 GC/MS. Some modifications to the inlet system, GC/MS, and analytical method were necessary to obtain an interface which produced acceptable results. For the analysis of field samples from Houston, Texas, the capillary inlet system was removed from the GC/MS and a Nutech Model 320 Thermal Desorption System, a commercially available unit similar to the capillary inlet system, was interfaced with the GC/MS. The Nutech unit was then used for the Houston field samples. Public Health Inititive analyses, and Cincinnati samples as, well as for blind-spike analyses to validate methodology.

EVALUATION

The capillary inlet system devised during analytical method development was initially installed on the GC of the Model 5985

GC/MS with the inlet system/GC interface maintained in its exact physical and functional configuration. Preliminary evaluations demonstrated that this system was operating properly with this configuration. These evaluations were performed by analyzing column test mixtures which were previously used to specify analytical performance during analytical method development (discussed in Section 6). Analyses of these mixtures were performed in the split injection mode, the mode used during method development, with injections made through a septum tee into an empty glass tube installed in the inlet system (see Figure 14, Section 6). Although the results demonstrated proper performance of the inlet system, the mass spectrometer was not as sensitive as the flame ionization detector (FID) used during method development. All of these experiments were performed with the mass spectrometer operated under electron impact ionization in a continuously scanning mode.

To improve analytical sensitivity, the inlet system was evaluated with very-low split and splitless injection operation. During splitless operation some compounds in the test mixtures were found to be catalytically altered. These *in situ* reactions were detectable with mass spectral information, but would not be identifiable with an FID (as previously used). Splitless operation also decreased the flow of carrier gas removing sample from the capillary inlet system trap. This extended the period of time to effectively transfer the sample from this trap to the GC and resulted in broadened chromatographic peaks, especially for low-boiling constituents. The problems of peak-broadening and catalytic alteration were found to decrease as the injection mode was changed from splitless to low-split to moderate-split operation. By periodically changing the nickel capillary trap of the inlet system, by maintaining uniform heating of the trap during desorption, and by adjusting instrument operating parameters, the problems of peak-broadening and catalytic alteration with splitless injection were found to be significantly reduced.

In order to provide authentic samples for final evaluation of the GC/MS analytical system for sorption tube analysis, samples were collected near the laboratory at Carillon Park in Dayton, Ohio. The details and sampling plan for this trip are presented in Section 8. Analyses were conducted using continuous scanning GC/MS and chromatographic procedures establishes during Phase II of this program. These analyses showed that the capillary GC/MS system should geneally be operated in a splitless mode in order to obtain suitable sensitivity.

Frequent adjustment, trap changing, and cleaning of the capillary inlet system were found to be necessary to maintain acceptable operation of the analytical system using this system and splitless operation. A commercial sample introduction system obtained previously was therefore interfaced to the Model 5985 GC/MS for the analysis of Houston field sample and those analyzed thereafter. The system was a Nutech 320 Thermal Desorption System and was composed of the same major elements as the original capillary inlet: thermal desorption chamber, heated valve, capillary trap, and thermal control unit. Sample reconcentration and introduction into the analytical systems were performed in the same manner; however, some of the physical details of these two systems varied. For example, the trap of the Nutech system was contained in such a manner that the thermal control unit controlled both the cooling and heating of this trap. This was an advantageous convenience. Both systems were found to perform satisfactorily.

Another change made prior to the analysis of the Houston field samples was to change the mode of sample introduction from splitless to direct injection. To accomplish this modification, the carrier flow directed to the sample introduction system (Nutech) was modified in the Model 5985 GC/MS system. Instead of being obtained from a split off of the capillary inlet pneumatics (see Figure 9, Section 6), the carrier gas was supplied from a separate auxiliary system with an independent pressure controller. Furthermore, instead of introducing a sample from the trap into the GC through a needle inserted in the GC injection port, a direct coupling was made between the Nutech system and the GC column. In the GC/MS this was done with glass-lined stainless steel tubing (passing through the GC injection port for heat) with low-dead-volume stainless steel connections to the Nutech system and capillary column. To accomodate potentially greater sample quantities, the capillary column within the GC/MS was changed from an ~50 M long, 0.2 mm ID, OV-101 fused-silica WCOT column to an ~60 M long, 0.25 mm ID, SE-30 glass WCOT column. (Both columns had non-polar, methyl-silicone liquid phases making them somewhat equivalent in chromatographic characteristics.) Carrier gas flow through the Nutech system directly passed into the capillary column. The flow rate of this carrier was controlled by the pressure controller of the auxiliary system.

RESULTS

As noted previously, analyses were conducted using a Hewlett-Packard 5985A GC/MS/Data System having a 50-meter fused silica column coated with methyl silicone liquid phase. This was later changed to a 60-meter glass capillary column having an equivalent phase. Chromatographic conditions were varied to meet the individual demands of specific samples. When possible, all sorbents from a single sampling run were analyzed using the same temperature program so that retention values could be compared. Samples collected in Dayton, Los Angeles and Niagara Falls were analyzed using the original capillary trap and inlet system designed and constructed as a part of this program (Section 6). Samples from Houston and those collected thereafter were analyzed using a Nutech Corporation Model 320 Thermal Desorption System. The latter unit was connected directly to the capillary analytical column of the GC/MS system. The two units offer essentially the same features; however, the Nutech system is more convenient to operate. This research effort was conducted with a companion program for the development of a multiresidue analysis for 20 carcinogens and screening techniques for the analysis of chemical class categories. Thus, in some instances, data from parallel sampling conducted under that program will be used to illustrate results pertinent to this project.

A basic premise of the multiple sorbent sampling approach is that, for ambient air sampling in the complex and often hostile environments frequently encountered, compounds of interest are often not completely retained by a single sorbent. This would be particularly true when the volume of air sampled is large. The results presented for the various locations sampled adequately demonstrate this fact.

Calibration for Compounds on the Twenty Potential Carcinogen List

Compounds on the list of twenty potential carcinogens being studied in this program, if found to be present, were quantitatively measured. Calibration was achieved by preparing sorbent tubes with known weights of each material using a standard gaseous Sample Generation System constructed at MRC. This system is based on controlled syringe injection, vaporization and subsequent serial dilution of the standard compounds (Appendix B). Quantification by GC/MS was achieved by integration of the peak corresponding to a major interference-free ion of the compound which appeared at the correct predetermined retention value.

Qualitative identification of other components was achieved by initially using a standard compilation of mass spectral data [9]. Several collections of complete mass spectra are available and were used for more detailed spectral analyses. In some cases, compounds have been identified by class and carbon number such as C_{10}-alkane or C_4-alkylbenzene. In the latter case, the total carbon number of the alkyl moieties is given. For the data obtained on the Houston samples, an attempt was made to identify the specific compounds where possible. Due to the similarity in fragmentation pattern of hydrocarbons under electron-impact, and because of the lack of strong molecular ions for highly branched hydrocarbons, boiling point data were used to select the one compound from several which might fit a mass spectrum.

Analysis of Sample Collected from Dayton Air

The Dayton site at which samples were collected was a woodland park that was considered to be relatively free of many of the objectionable organic materials. Its proximity to a heavily travelled major highway however may have contributed to the hydrocarbon level. Results from analysis of a Tenax collector are presented in Table 41. A reconstructed total ion chromatogram from that analysis is presented in Figure 34. The number shown by each response refers to a compound listed in Table I. Only three of the twenty evaluation compounds were found in this sample, these being benzene, tetrachloroethylene and styrene. As noted earlier in this section, the primary purpose for collecting the Dayton samples was to provide authentic specimens for evaluation of the analytical system, thus the analysis was only qualitative in nature. Moreover, some of the detected compounds such as a series of silicone species are known to originate from within the system. These result from either analytical column bleed or from residues of silanizing reagent.

Chromatograms obtained from the Porapak R and Ambersorb tubes, located in the second and third positions in the sorbent series, showed minor amounts of paraffinic hydrocarbons as the only compounds present.

The Dayton field tests, demonstrated that the analytical system was a viable one. These tests permitted a number of adjustments to be made to improve the background and performance of the system.

Los Angeles Air Sampling Analysis

The atmospheric conditions and the sampling location in metropolitan Los Angeles are given in Section 8 of this report.

Figure 35 presents the chromatograms (total ion current plots) of materials retained on each of the sorbents from a single sampling run. The chromatogram at the bottom of the figure shows compounds retained in the Tenax-filled collector, while chromatograms for materials from the Porapak R and Ambersorb XE-340 collectors are shown in the middle and upper parts of the figure. At the top of the figure, a chromatogram of the contents of the backup Ambersorb XE-340 collector is shown.

By comparing the compounds retained by each of the sorbents, it is apparent that many compounds of interest escape collection on the Tenax and are retained in the Porapak and Ambersorb collectors. Benzene, for example, appears largely in the latter two collectors. Tetrachloroethylene, while appearing in the Tenax collector, is heavily concentrated in the Porapak R collector. Both of these compounds are included among the twenty potential carcinogens selected for evaluation in this program. Another compound of some interest is trichloroethane. This compound is found to reside essentially in the Ambersorb and Porapak R collectors.

Sampling system break-through is found to be minimal as shown by analysis of the Ambersorb backup collector which is the fourth tube in the collection series. The single, large peak observed from this collector is due to carbon dioxide.

TABLE 41. COMPOUNDS DETECTED IN AMBIENT AIR SAMPLES COLLECTED IN DAYTON

Compound	Reference number[a]
Carbon dioxide	1
Methylene chloride	2
Trimethylsilanol	3
Benzene	4
Silicone specie[b]	5
C_7-Alkane	6
C_8-Alkane	7
Toluene	8
C_8-Alkanes	9
Tetrachloroethylene	10
C_8-Alkane	11
Silicone species[b]	12
Ethylbenzene	13
Xylene	14
Styrene	15
Xylene	16
C_9-Alkane	17
Cumene	18
n-Propylcyclohexane	19
Benzaldehyde	20
C_3-Alkylbenzenes	21
C_9-Alkane	22
C_3-Alkylbenzenes	23
C_{10}-Alkane	24
Silicone specie[b]	25
C_4-Alkylbenzene	26
Ethylstyrene	27
Ethylstyrene	28
C_{11}-Alkane	29
Silicone species[b]	30
Dimethylindan	31
Silicone specie[b]	32
C_{12}-Alkane	33
C_{13}-Alkane	34
Silicone specie[b]	35
C_{13}-Alkane	36

[a] Peak number from total ion chromatogram shown in Figure 34.

[b] Silicone components probably due to system silanization and/or column bleed.

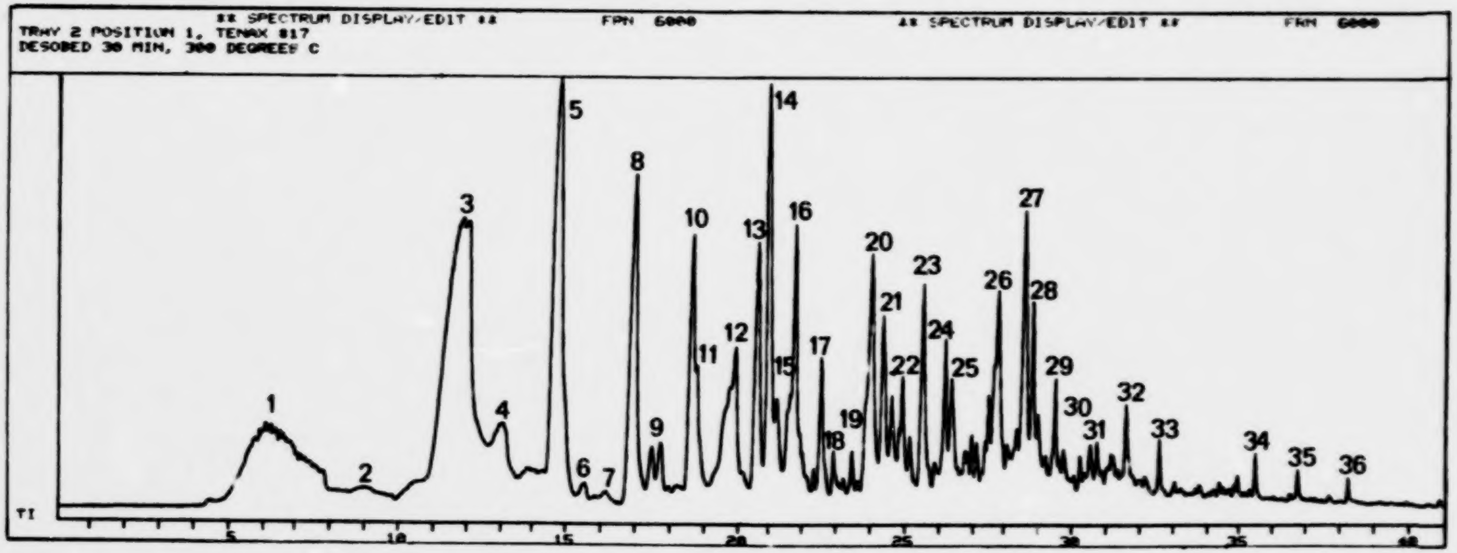

Figure 34. Reconstructed total ion chromatogram of Tenax Collector Sample from Dayton Sampling.

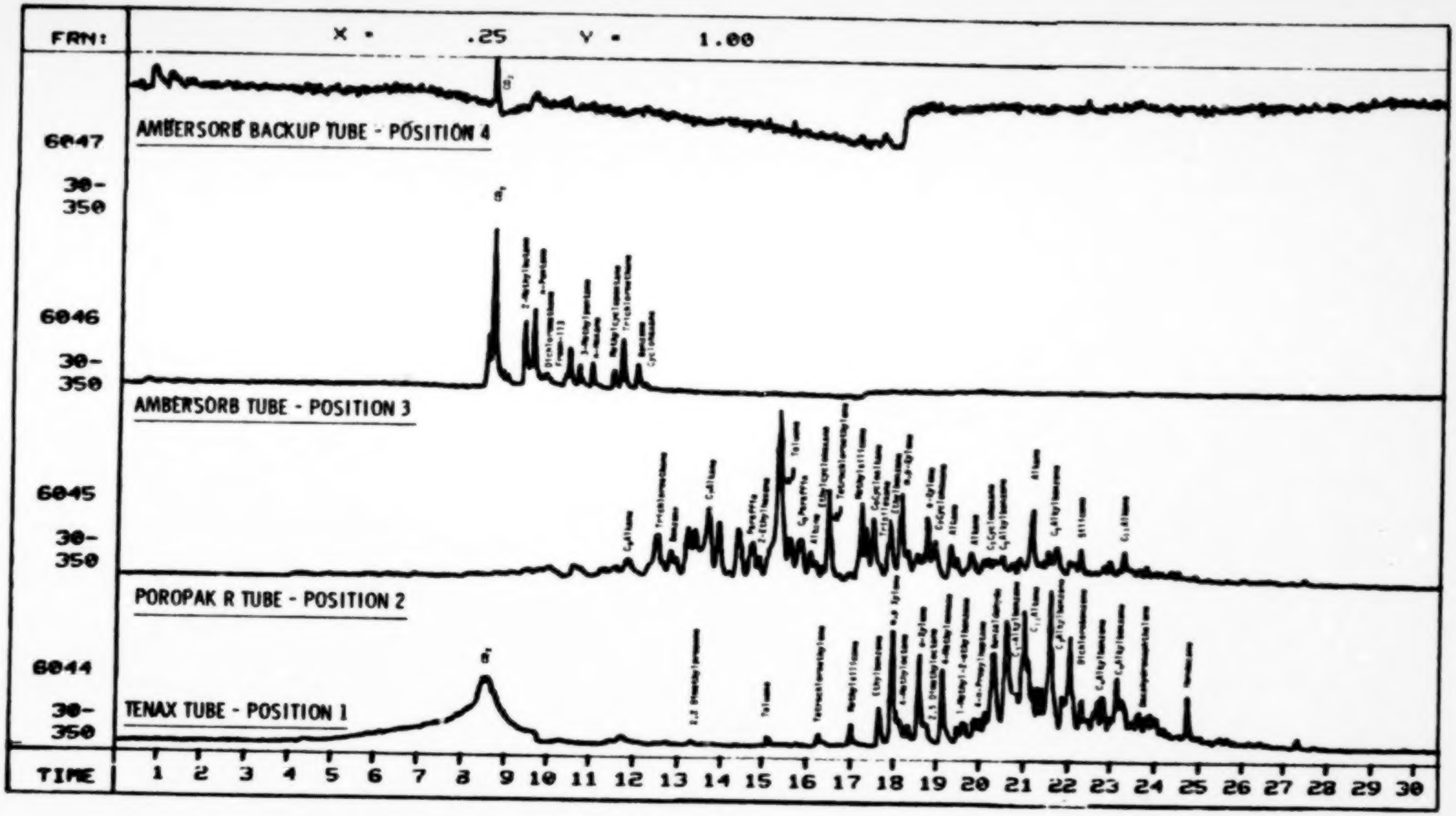

Figure 35. Reconstructed total ion chromatogram of materials collected in metropolitan Los Angeles by the multisorbent air sampling technique.

The chromatograms in Figure 35 are normalized on the intensity of the strongest peak in each chromatogram. For quantitative comparison of one chromatogram to any of the others shown in that figure, absolute intensities must, of course, be compared. Accordingly, absolute peak area counts were used as the basis for the foregoing observations. Table 42 presents the amount of benzene and tetrachloroethylene found in each sorbent tube and the concentration of these compounds in the sampled air.

TABLE 42. SUBJECT COMPOUNDS PRESENT IN SAMPLES COLLECTED IN METROPOLITAN LOS ANGELES

Compound	Weight per collector, ng			Total weight, ng	Concentration,[a] ng/m^3 in air
	Tenax-GC	Porapak R	Ambersorb		
Benzene	11	55	9	75	214
Tetrachloroethylene	24	37	-	61	174

[a] 350 liters of air sampled.

Niagara Falls Air Sampling Analysis

Sampling conducted in Niagara Falls, New York was of particular interest to this program because it provided a rather sheltered sampling environment. Sampling was conducted indoors where atmospheric oxidants (ozone, NO_x) were presumably at a low level, temperature and humidity were moderate, and the contribution to the sample matrix by various common mobile and stationary emission sources was minimal. The unattended performance of the sampling systems was tested and several improvements in the system were made as a result of observed deficiencies. The need to draw a moderate flow of air through four in-series sorbent tubes places a heavy demand upon a sampling pump. The pressure drop across the multiple-sorbent collector system has a tendancy to cause the drive belt of the DuPont P3000 pump to either break or disengage from its pulley. For unattended sampling, the drive belt cannot be immediately replaced so the sample is lost, as was the case for one of the Niagara Falls samples. The normal pressure drop over the sorbent train is about two inches of mercury, though for at least one set of tubes, it was as high as six inches of mercury. In order to reduce the pressure drop, as well as its variability, the sorbent tube size was modified to give a larger bed cross section while maintaining the same bed volume. The inside diameter of air tube was increased from 10 mm to 13 mm. This was found to reduce the pressure drop significently and to make it more constant. The larger diameter tube is discussed in the Operation Manual, Appendix A.

Though the purpose of the Niagara Falls, N.Y. sampling was to quantitate three specific compounds, benzene, tetrachloroethylene and trichloroethylene, all twenty potential carcinogens were included in the data evaluation. A total ion chromatogram of the contents of a Tenax collector is presented in Figure 36. A list of detected compounds is keyed by peak number to this chromatogram and is given in Table 43. As is shown by the chromatogram, the sample size significantly exceeded the capacity of the column, resulting in broadened chromatographic peaks. An important finding, however, was that even with the high sample loading and the large volume of air sampled, no sample breakthrough to the other sorbents in the series occurred. Total ion chromatogram from analyses of the Porapak R and Ambersorb tubes show that no breakthrough of air components has occurred.

Quantitation of four compounds among the twenty subject potential carcinogens was conducted and is presented in Table 44.

Houston Air Sample Analysis

The results from the Niagara Falls, New York sampling indicated that sample breakthrough, and the resultant need for the multisorbent sampling system, may depend upon sample matrix and/or sampling conditions. To further evaluate this possibility, a field sampling trip was scheduled to take place in Houston, Texas during a sustained period of record high temperatures, accompanied by high humidity. During the time of actual sampling, the temperature ranged in the nineties and relative humidity was $\sim$90%.

Several modifications in the analytical system were made prior to analysis of the collected samples. Since a heavy loading of compounds was expected in these samples, the narrow-bore, fused-silica GC capillary column was replaced with a similar larger-bore glass column of about the same length. A methyl silicone liquid phase was retained. The capillary trapping and inlet system of MRC design, was replaced with a Nutech Model 320 Thermal Desorption System. Since the collection tubes used for the ambient air sampler differed from those designed for the Nutech Model 320, an external desorption furnace was connected to the Model 320.

The extremes in humidity presented a problem in the analysis of the Porapak and Ambersorb collector contents. Best results were obtained in previous analyses by maintaining the gas chromatograph column at -30°C during warming of the cryogenic trap. This procedure insured that all trap contents would be on the head of the column before any component began to travel through the column. The large amount of water present in the latter collectors, once condensed, tended to block the column or pass as droplets of water through the column. No data could be obtained under these conditions. By modifying the analytical conditions so that the column was maintained at +30°C during the trap warming cycle, water did not condense and an adequate analysis was possible.

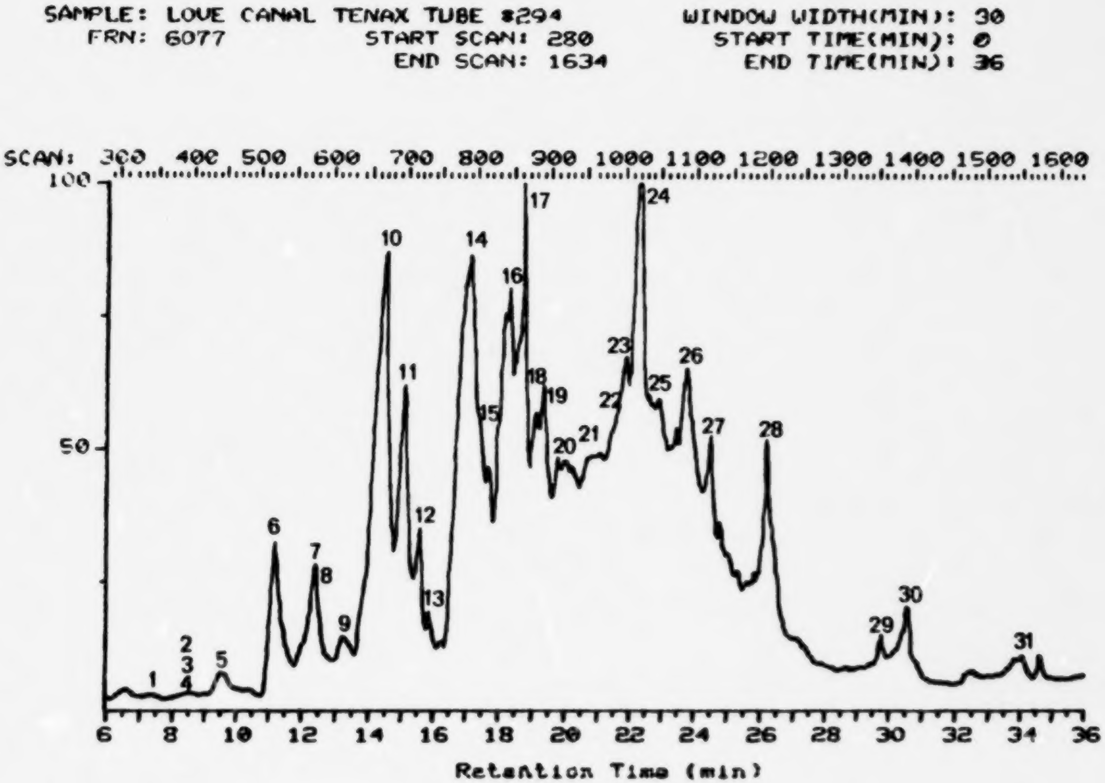

Figure 36. Qualitative scan of a Tenax collector sample from Niagara Falls sampling with the Portable Miniature System.

TABLE 43. COMPOUNDS DETECTED IN AMBIENT AIR SAMPLES COLLECTED IN INDOORS AT NIAGARA FALLS, N.Y.

Compound	Reference number[a]
1,1,1-Trichloroethane	1
Benzene	2
Cyclohexane	3
Carbon tetrachloride	4
Dimethylpentane	5
Toluene	6
Perchloroethylene	7
C_8-Alkane	8
Chlorobenzene	9
Xylene	10
Xylene	11
C_9-Alkane	12
Trimethylbenzene	13
o-Chlorotoluene	14
Acetophenone	15
C_3-Alkylbenzene	16
Silicone specie[b]	17
C_4-Alkylbenzenes	18
Dichlorobenzene, m/p	19
C_4-Alkylbenzene	20
C_{11}-Alkane	21
C_{11}-Alkane	22
C_4-Alkylbenzenes	23
Dichlorotoluene	24
Dichlorotoluene	25
Silicone specie[b]	26
C_{12}-Alkane	27
Silicone specie[b]	28
Silicone specie[b]	29
Silicone specie[b]	30
Silicone specie[b]	31

[a] Peak number from total ion chromatogram shown in Figure 36.

[b] Probably from system silanization.

Total ion chromatograms for the Tenax and Porapak collectors are shown in Figures 37-38. Retention values for the various analyses vary because of the change in chromatographic conditions. Components present in the Tenax and Porapak collectors are tabulated and presented in Tables 45 and 46. No component breakthrough into the Ambersorb tubes occurred.

TABLE 44. SUBJECT COMPOUNDS DETECTED IN SAMPLES COLLECTED INDOORS AT NIAGARA FALLS

Compound	Mass,[a] ng	Volume air sampled, liters	Concentration, ng/m^3
Benzene	1,270	295	4,305
Tetrachloroethylene	1,720	295	5,830
Benzyl chloride	1,010	295	3,424
Carbon tetrachloride	950	295	3,220

[a] Entire amount retained in the first sorbent tube which contained Tenax GC.

Only benzene and tetrachloroethylene, of the list of twenty potential carcinogens, were detected in the Houston ambient air samples. The distribution of these components between the various sorbents is presented in Table 47.

Public Health Inititive Analyses

a. Analysis of Blind Spikes

In order to refine and validate the analytical methodology used in this program sorbent tubes spiked with fixed amounts of the public health inititive compounds were analyzed. These compounds are listed in Table 48 and their reconstructed total ion chromatogram is shown in Figure 39. Tenax GC and Porapak R Collection tubes were sent to Research Triangle Institute, RTP, North Carolina where "blind" spikes were prepared. Information on the amount of material spiked onto the tube was furnished to MRC only after completion of the analyses. At that time, data were exchanged, i.e., analytical values were traded for spike information. The standard sample generation system described in Appendix B was used at MRC to prepare calibration standards for use in the GC/MS analysis of the spiked sorbent. Both internal and external standards were used in the analyses. Hexafluorobenzene and octofluorotoluene were used as internal standards and a mixture containing all ten of the compounds of interest, in equal amounts by weight, was used to generate standards on Tenax sorbent. Three 600 ng standards, two at four hundred ng and three at 200 ng were prepared. After recording data for each standard by GC/MS, average responses were used to calculate linear equations by the least-squares method. Correlation coefficients, computed using four points, consisting of three standards and the origin, are listed in Table 49 for each compound.

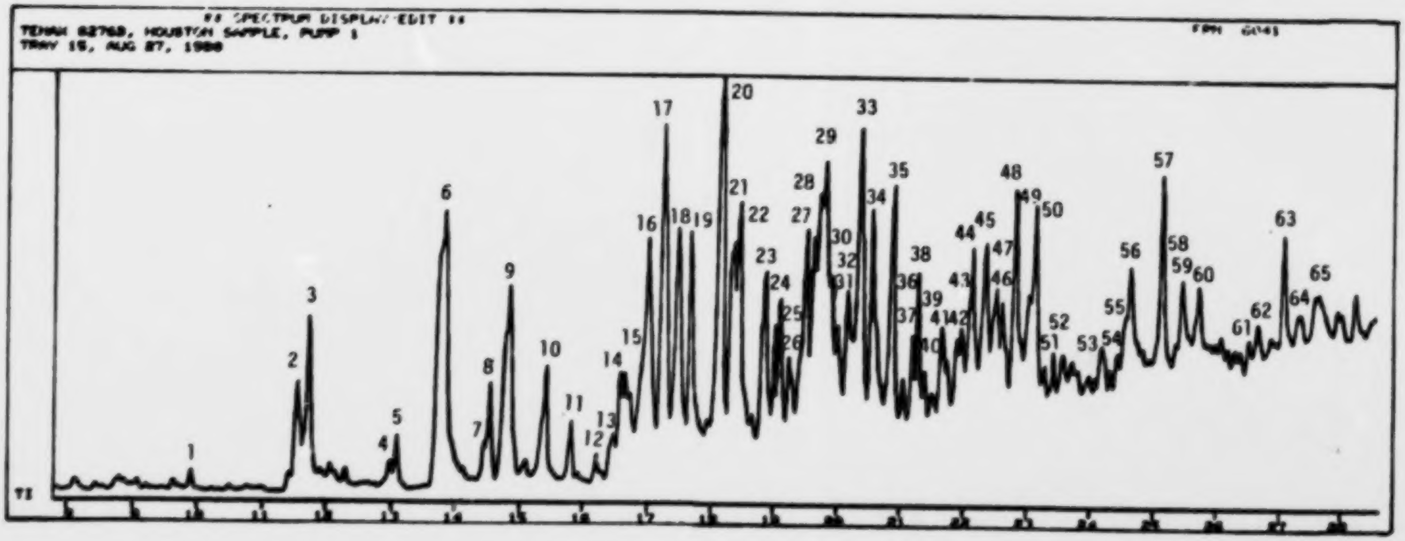

Figure 37. Reconstructed total ion chromatogram of compounds collected in Houston on Tenax-GC using the portable miniature collection system.

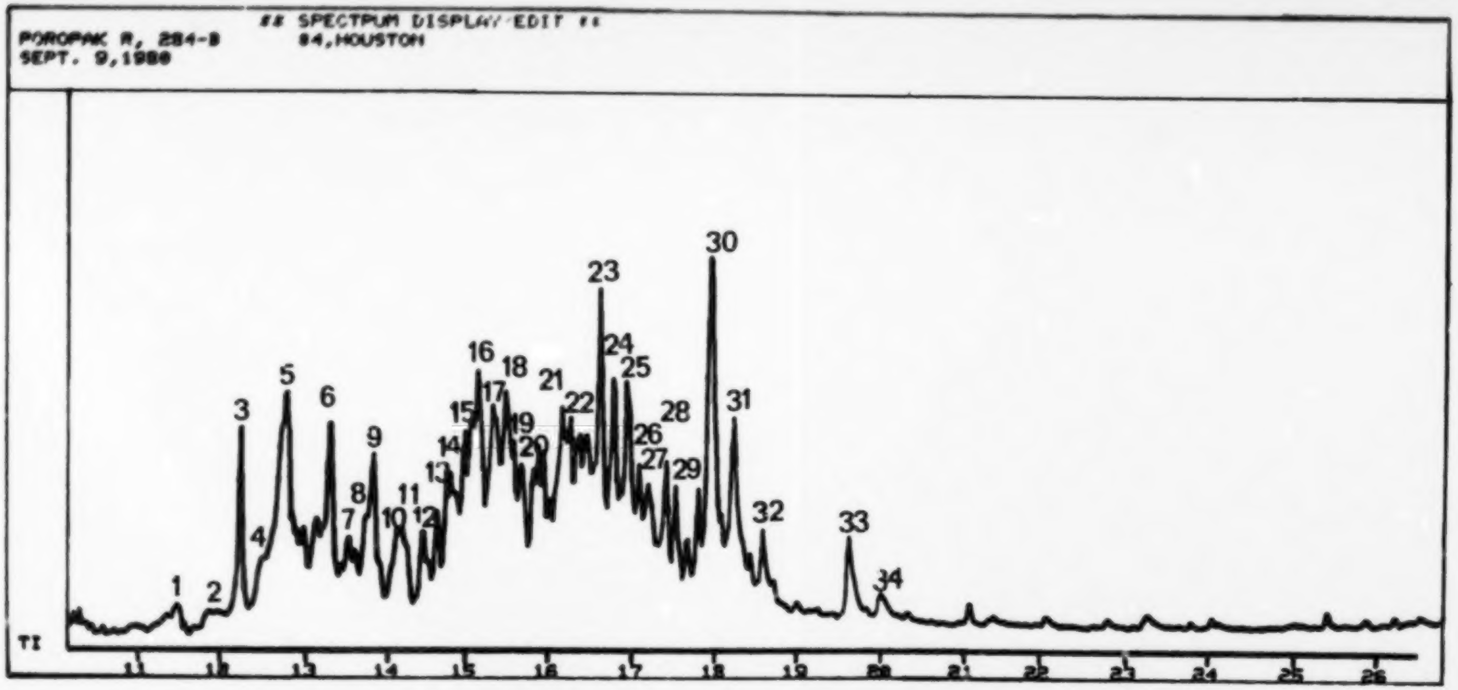

Figure 38. Reconstructed total ion chromatogram of materials collected on Porapak R collector in Houston, Texas.

TABLE 45. COMPOUNDS COLLECTED ON TENAX DURING HOUSTON SAMPLING (PEAKS OF CHROMATOGRAM SHOWN IN FIGURE 37)

1. C_7-Alkane
2. C_7-Alkane
3. Toluene
4. C_8-Alkane
5. C_8-Alkane
6. Silicones*
7. Silicones*
8. Ethylbenzene
9. Xylenes, m,p-
10. Xylene, O-
11. C_9-Alkane
12. C_3-Alkylbenzene
13. Alkanes
14. Acetic acid
15. Alkane
16. C_3-Alkylbenzene
17. C_3-Alkylbenzene
18. C_3-Alkylbenzene
19. C_3-Alkylbenzene
20. C_3-Alkylbenzene
21. Silicone*
22. Dichlorobenzene
23. C_{10}-Alkane
24. C_{10}-Alkane
25. Indane
26. n-Butylcyclohexane
27. Phenol
28. C_4-Alkylbenzene
29. C_4-Alkylbenzene
30. Acetophenone
31. Alkane
32. Dimethylethylbenzene
33. Ethylstyrene
34. Ethylstyrene
35. C_{11}-Alkane
36. Divinylbenzene
37. C_4-Alkylbenzene
38. C_4-Alkylbenzene
39. C_4-Alkylbenzene
40. C_{12}-Alkane
41. 1-Methylindane
42. 2-Methylindane
43. Benzylacetate
44. Silicone*
45. C_4-Alkylbenzene
46. 2-Phenyl 2 Methylbutane
47. C_4-Alkylbenzene
48. Naphthalene
49. Menthol
50. C_{12}-Alkane
51. Alkane
52. Benzothiazole
53. Dimethylacetophenone
54. Methyltetrahydronaphthalene
55. Benzoic acid
56. Dimethylindan
57. 2-Methylnaphthalene
58. Ethylcumene
59. 1-Methylnaphthalene
60. Silicone*
61. C_{13}-Alkane
62. Biphenyl
63. C_{14}-Alkane
64. C_{14}-Alkane
65. Dimethylnaphthalene

*Artifact peaks from system silanization and/or analytical column bleed.

Contained in that table, also, are precent standard deviation values for the three 600 ng standards. These data indicate that a reliable calibration, which is linear over the range of interest, has been obtained. The internal standards (perfluoro-, benzene and -toluene) were used to correct for short term instrument variations between calibration runs.

TABLE 46. COMPOUNDS DETECTED IN AMBIENT AIR SAMPLES COLLECTED AT HOUSTON PORPAK R COLLECTOR

Compound	Reference number[a]
Acetic acid	1
Benzene	2
C_7-Alkanes	3
C_8-Alkanes	4
Toluene	5
Silicone specie[b]	6
Methylcyclohexane	7
Ethylbenzene	8
Xylene	9
Xylene	10
Methylethylocyclohexane	11
C_9-Alkane	12
C_9-Cycloalkane	13
4-n-Propylheptane	14
C_{10}-Alkane	15
Diethylcyclohexane	16
Silicone specie[b]	17
Methylisopropylcyclohexane	18
C_{10}-Cycloalkane	19
C_3-Alkylbenzene C_{10}-Alkane	20
n-Butylcyclohexane	21
Methylfurylketone	22
Decalin	23
Dimethylstyrene	24
Ethylstyrene	25
Tricyclodecane	26
C_9-Diketone	27
Diethyl phenol	28
Methyldecalin Methyl t-butylphenol	29
o-Allylphenol	30
Ethylbenzaldehyde	31
Alkane	32
Dimethylacetophenone	33
Ethyl acetophenone	34
Silicone specie[b]	35
Alkane	36

[a] Refers to reconstructed total ion chromatogram shown in Figure 38.

[b] Silicone components apparently due to system silanization and/or column bleed.

TABLE 47. SUBJECT COMPOUNDS PRESENT IN SAMPLES COLLECTED IN HOUSTON, TEXAS

Compound	Weight per collector, ng Tenax-GC	Porapak R	Ambersorb	Total weight, ng	Concentration,[a] ng/m^3 in air
Benzene	73	17	-	95	327
Tetrachloroethylene	28	-	-	28	96

[a] 290 liters of air sampled.

The calibration and analysis of spiked samples could not be initiated immediately upon receipt of the spikes due to minor instrument problems. Consequently, the age of the spikes at the time of analysis was well beyond the recommended storage time for that type of sample. Nevertheless, analyses were conducted as planned and results are presented in Table 50. As noted in the table, the Porapak R spike gave reasonable results for some compounds, however, other of the less volatile constituents were not very effectively desorbed. The age of the spike-samples was doubtlessly an important factor affecting the overall analytical results, as higher boiling compounds appeared to be irreversibly absorbed even on the Tenax sorbent.

A second set of spiked tubes were prepared by RTI and analysis of these, using essentially the same procedure, gave the results shown in Table 51. These analyses show much better agreement with spiked values having an average deviation from the spiked amount of only 21.9%.

b. Personnel Sampling and Analysis for Public Health Inititive Compounds

The miniature portable sampling system was used to collect samples over a three-day period, October 29-31, at Research Triangle Park. The system was worn by a worker within the EPA Offices at RTP and was taken home with him in order that 24-hour exposure sampling could be acquired. Analysis of the sorbent tubes showed that under the prevailing sampling conditions, no sample breakthrough was observed. All material remained on the Tenax sorbent. Table 52 presents the analysis of the Tenax tubes for the public health initive compounds. It will be noted that one collector was spiked with 400 ng of each compound before tubes were shipped from the laboratory. Analyses show that, particularly in the case of higher volatile compounds, some material has been lost. The materials were not swept from the tube during sampling since they did not appear in either the Porapak R or Ambersorb tubes. Data are present in Table 53 for additional compounds present in these samples. An estimate of the amount of each compound present has been made.

TABLE 48. PUBLIC HEALTH INITITIVE COMPOUNDS

		Boiling point, (°C)	Retention time, (min)	Major Mass lines, m/e		
1.	Chloroform	61	7.76	83	85	47
2.	1,2-Dichloroethane	83	8.45	62	49	64
3.	1,1,1-Trichloroethane	74	8.48	97	99	61
4.	Benzene	80	8.90	78	52	
5.	Carbon tetrachloride	77	9.04	117	119	121
6.	Trichloroethylene	87	10.05	95	130	132
7.	Bromodichloromethane	89	10.16	83	85	47
8.	1,1,2-Trichloroethane	113	11.95	97	83	85
9.	Tetrachloroethylene	121	13.20	166	164	129
10.	Chlorobenzene	131	14.15	112	77	114

Some surprisingly high levels of compounds were detected as shown by the table of "additional compounds." Napnthalene in several cases falls into the 1500-10,000 ng/m^3 range, as does limonene and α-pinene. All three of these materials may originate from sanitary products or the latter two could originate from natural sources, such as from conifers. It is noteworthy that despite high loadings of organics no breakthrough was detected.

The results presented indicate that components can breakthrough a single Tenax collector under certain conditions. Though all of the factors involved have not been fully defined, it is clear that sampling volume is involved but is not the only factor. Climatic conditions such as temperature and humidity, as well as the composition of the sample, are doubtlessly factors as well. For very low volumes of sample, breakthrough would not be expected. The continually increasing need for lower detection limits, however, requires that a large volume of air be sampled to assure sufficient material for analyses. The data obtained during the Niagara Falls sampling shows that, even with a large volume, Tenax may retain all of the organic constituents under certain conditions. The sample volume taken at that location was greater than that taken during Houston sampling and nearly as great as that taken at Los Angeles. Moreover, the loading of the specific compounds of interest was greater than that found at the other locations.

Compound retention on Tenax sorbent may be affected by other factors, the evaluation of which is beyond the scope of this program. These may include selective displacement effects by other matrix compounds; interaction with water whereby an immiscible compound pair, having a combined vapor pressure higher

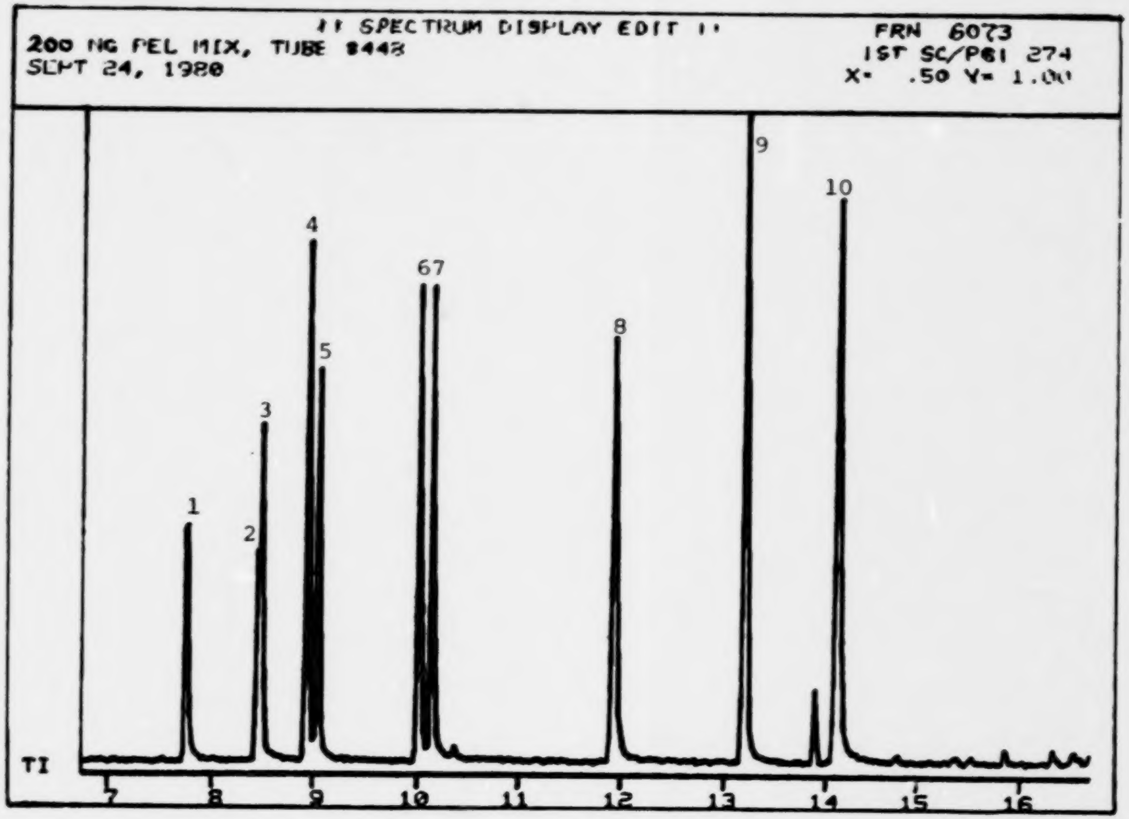

Figure 39. Reconstructed total ion chromatogram of Public Health Inititive Compounds - 200 ng each.

TABLE 49. EVALUATION OF CALIBRATION DATA

Compound	Correlation coefficient for four calibration points	Percent standard deviation for 3-600 ng standards
Chloroform	0.994	2.4
1,2-Dichloroethane	0.988	5.2
1,1,1-Trichloroethane	0.991	7.7
Benzene	0.990	7.8
Carbon tetrachloride	0.997	5.0
Trichloroethylene	0.988	3.6
Bromodichloromethane	0.995	3.2
1,1,2-Trichloroethane	0.908	11
Tetrachloroethylene	0.998	9.3
Chlorobenzene	0.989	5.2

than that of either compound (as in steam distillation) is formed; change in the surface characteristics of the Tenax due to atmospheric constituents such as ozone or NO_x.

Except under certain very controlled or specific conditions the multisorbent sampling approach is required to assure complete retention of all compounds.

The methodology developed during the course of this program has been applied to a wide variety of potential carcinogens to demonstrate its effectiveness as a screening technique. As noted previously, certain artifact compounds have been found in most of the samples. Some of these, such as the silicones, are recognized as originating from the analytical system. Great importance has been placed on the recognition of artifact peaks only if the compound is environmentally significant.

TABLE 50. ANALYSIS OF SPIKE SET #1

Compound	Analysis of spikes on Tenax (nanograms) #1	#2	#3	Relative standard deviation	Nanograms: Mean value	Spiked value	Percent deviation from spike	Analysis of Porapak R spike (nanograms)
Chloroform	142	125	129	6.7	133	85	56	138
1,2-Dichloroethane	327	264	248	15	279	239	17	30
1,1,1-Trichloroethane	430	390	405	4.9	408	198	106	452
Benzene	290	235	273	10.6	266	221	20	277
Carbon tetrachloride	255	208	213	11.2	231	147	57	(105)[a]
Trichloroethylene	356	289	308	10.9	317	301	5	(60)
Bromodichloromethane	90	77	65	15.8	77	94	18	(ND)
1,1,2-Trichloroethane	<25	<25	<25	-	<25	66	(62)	(ND)
Tetrachloroethylene	170	130	167	13.4	166	232	28	(108)
Chlorobenzene	75	52	68	18.1	65	96	32	(49)

[a] Though bracketed numbers have been generated, in the multisorbent system these compounds would be analyzed on Tenax due to their poor desorption characteristic on Porapak R.

TABLE 51. ANALYSIS OF RTI SPIKE SET #2

Compound	Spiked Tenax tubes #1	#2	#3	#4	#5	Average	Spiked value	Percent deviation
Chloroform	89	87	96	93	92	91	97	6.2
1,2-Dichloroethane	216	218	228	238	212	222	228	2.6
1,1,1-Trichloroethane	195	189	-	208	187	194	134	44.8
Benzene	237	235	230	214	234	230	217	6.0
Carbon tetrachloride	196	192	205	219	186	199	145	37.2
Trichloroethylene	242	249	262	273	227	250	284	12.0
Bromodichloromethane	68	64	68	68	72	68	88	22.7
1,1,2-Trichloroethane	46	33	32	44	49	41	64	35.9
Tetrachloroethylene	162	165	144	213	148	166	241	31.1
Chlorobenzene	72	48	47	84	36	57	72	20.8
						Average Deviation		21.9

TABLE 52. TARGET COMPOUNDS COLLECTED AT RTP DURING PERSONNEL MONITORING OF EPA EMPLOYEE

	ng/m^3					
	#1	#2	#3	#4[a]	#5[b]	#6
Chloroform	1000	129	-	261	-	36
1,2-Dichloroethane	-	-	-	580	-	-
1,1,1-Trichloroethane	352	260	918	1669	46	290
Benzene	727	412	402	1000	-	384
Carbon tetrachloride	174	140	177	1000	-	95
Trichloroethylene	178	120	30.6	1214	-	32
Bromodichloromethane	-	-	-	598	-	-
1,1,2-Trichloroethane	-	-	-	1308	-	-
Tetrachloroethylene	794	422	3780	3150	33	364
Chlorobenzene	-	-	-	1670	-	-
Volume sampled, liters	224	490	485	240	-[b]	445
Sampling period						
Date	10/29	10/29	10/30	10/30	10/30	10/31
Hours	1830-2214	2215-0645	0730-1540	1835-2215	2233-0645	0712-1440

[a] Tube #4 was spiked with 400 ngs of each compound prior to shipment to RTP.

[b] Pump belt broke during this sampling.

TABLE 53. ADDITIONAL COMPOUNDS DETECTED IN RTP PERSONNEL MONITOR SAMPLES

	Estimated level[a]					
	Tenax sample					
Compounds	#1	#2	#3	#4	#5[b]	#6
1,1,2-Trichloroethane	-	-	-	2	-	-
2-Methyl 1,3-butadiene	2	-	2	2	-	-
Acetone	2	2	2	-	-	2
C_5 & C_6 Alkanes	2	2	2	-	-	2
3-Methylpentane	2	2	2	-	-	2
Chloroform	2	1	-	2	-	1
Benzene	2	2	2	2	-	2
C_7-Alkane	1	2	2	2	-	2
Trichloroethylene	1	1	1	1	-	1
Mesityl oxide	1	-	2	-	-	1
Toluene	3	2	2	3	1	3
Tetrachloroethylene	2	2	3	3	1	2
Carbon tetrachloride	1	1	1	2	-	1
Bromodichloromethane	-	-	-	2	-	-
Chlorobenzene	-	-	-	2	-	-
C_8-Alkane	1	2	1	-	-	-
Ethylbenzene	-	1	1	2	-	2
Xylene(s)	-	2	2	3	1	2
Styrene	2	1	1	2	1	2
α-pinene[c]	2	1	2	2	-	3
Benzaldehyde	2	1	-	2	-	1
C_3-Alkylbenzene	1	1	-	-	1	2
Tolualdehyde	-	1	-	-	-	1
Dichlorobenzene	1	1	1	2	-	3
Limonene	2	3	-	2	-	3
C_4-Alkylbenzene	2	-	-	1	-	2
Methylene chloride	2	-	2	-	-	1
1,1,1-Trichloroethane	1	2	2	2	1	2
Naphthalene	1	1	-	3	1	3
1,2-Dichloroethane	-	-	-	2	-	-
Air volume sampled, liters	224	490	485	240	-[b]	445

[a] 1 = 1-300 ng/m^3
2 = 300-1500 ng/m^3
3 = 1500-10,000 ng/m^3.

[b] Inadequate sample obtained due to pump failure.

[c] Sample #4 spiked at 400 ng level with each target compound.

Analysis of Personnel Air Monitoring Samples from Cincinnati Sampling Trip

In order to compare the results of sampling at RTP with those of another area, personnel monitoring samples were taken in Cincinnati, largely indoors. Two of the target compounds were observed to breakthrough the first tube packed with Tenax-GC into the second tube filled with Porapak R. Of the two compounds, benzene and perchloroethylene, a small amount of the former appeared in the first ambersorb tube. No break-through into the second ambersorb tube occurred. Since the sampling was conducted for the entire duration an autombile try from Dayton, Ohio to Cincinnati, automotive exhaust from Interstate Route 75 traffic was doubtlessly included in the sampling.

Results of the analyses of target compounds are presented in Table 54. The reconstructed total ion chromatogram from analyses of the Tenax tube is presented in Figure 40 and the identification of compounds represented by the peaks in that chromatogram are listed in Table 55. Figure 41 illustrates the total ion chromatogram obtained from the Porapak collector (second in the series) while Figure 42 shows the chromatogram obtain from the first Ambersorb collector (third in the series). The compounds identified in the Porapak and Ambersorb collectors are listed in Table 56.

TABLE 54. TARGET COMPOUNDS COLLECTED AT CINCINNATI DURING PERSONNEL MONITORING OF MRC EMPLOYEE

Compound	Weight per collector			Total weight, hg	Concentration[a], ng/m^3 in air
	Tenax GC	Porapak R	Ambersorb[b]		
Benzene	953	60	19	1,032	2,948
Tetrachloroethylene	463	9	-	472	1,348
Carbon tetrachloride	32	-	-	32	91
Trichloroethylene	8.4	-	-	8.4	24

[a] 350 liters of air sampled.

[b] Second Ambersorb tube (back-up) contained no compounds.

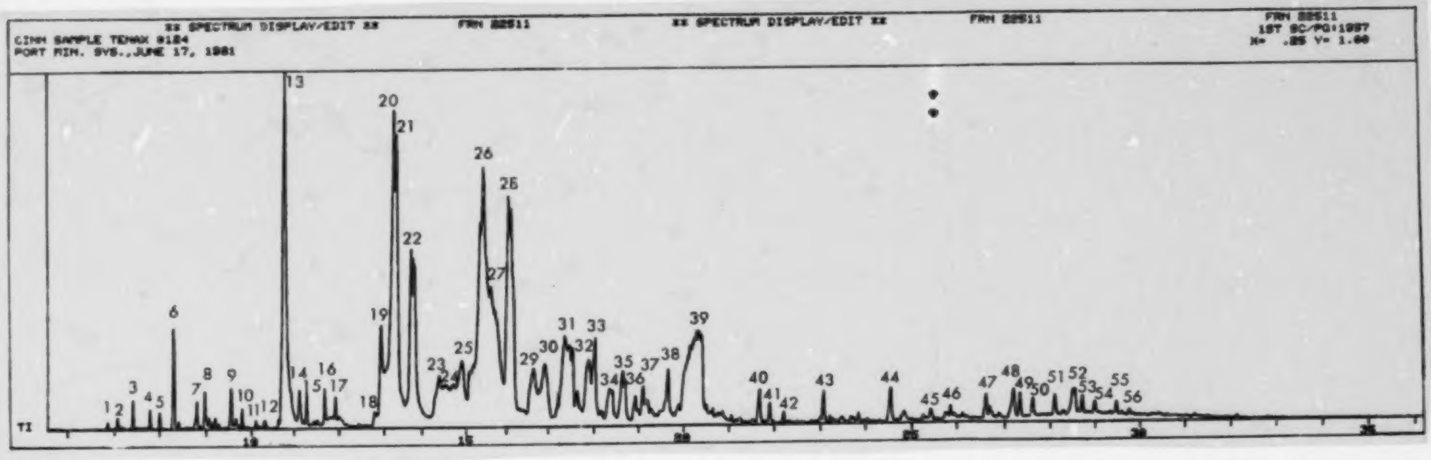

Figure 40. Reconstructed total-ion chromatogram of Personnel Monitoring Sample collected in Cincinnati, Tenax collector.

TABLE 55. MAJOR COMPONENTS DETECTED IN PERSONNEL MONITORING SAMPLE COLLECTED IN CINCINNATI

Peak number[a]	Compound	Peak number[a]	Compound
1	2-Methylpentane	28	C_3-Alkylbenzene(s)
2	3-Methylpentane	29	C_3-Alkylbenzene(s)
3	Hexane	30	C_{10}-Paroffin
4	Methylcyclopentane	31	C_4-Alkylbenzenes
5	Ethylene chloride	32	C_4-Alkylbenzenes
6	Benzene	33	C_4-Alkylbenzenes
7	2-Methylhexane	34	C_4-Alkylbenzene and C_{11}-paroffin
8	Trimethylpentane	35	C_4-Alkylbenzene
9	n-Heptane	36	2-Ethenyl-1,3-dimethylbenzene
10	Methylcyclohexane	37	2,3-Dihydro-4-methylindene
11	Ethylcyclopentene	38	Naphthalene
12	Methylheptene	39	Silicones[b]
13	Toluene	40	1-Methylnaphthalene
14	2-Methylheptane	41	2-Methylnaphthalene
15	3-Methylheptane	42	Paraffinic hydrocarbon
16	Tetrachloroethylene	43	Silicone[b]
17	Octane	44	2,5-Cyclohexadiene-1,4-dione, dimethyl ethyl
18	Silicone[b]	45	Paraffinic hydrocarbon
19	Ethylbenzene	46	Silicone specie[a]
20	*p*-Xylene	47	Butyric acid ester
21	*m*-Xylene	48	Butylheptylbenzene
22	*o*-Xylene	49	Propyloctylbenzene
23	Dimethyl heptane	50	C_{11}-Alkylbenzene
24	Nonane	51	Methyldecylbenzene
25	Butoxyethanol	52	Pentylheptylbenzene
26	C_3-Alkylbenzene(s)	53	C_{12}-Alkylbenzene
27	C_3-Alkylbenzene(s)		

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[a] Refers to peak number in chromatogram of Figure 40.

[b] Artifact peaks resulting from system silation.

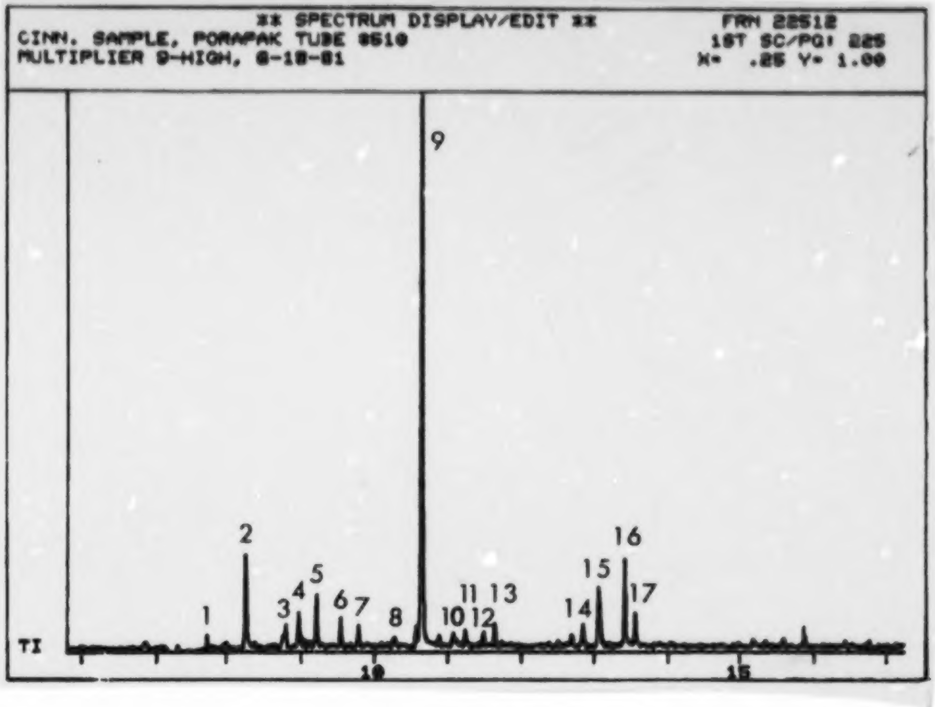

Figure 41. Reconstructed total ion chromatogram of Porapak collector contents, Cincinnati sampling.

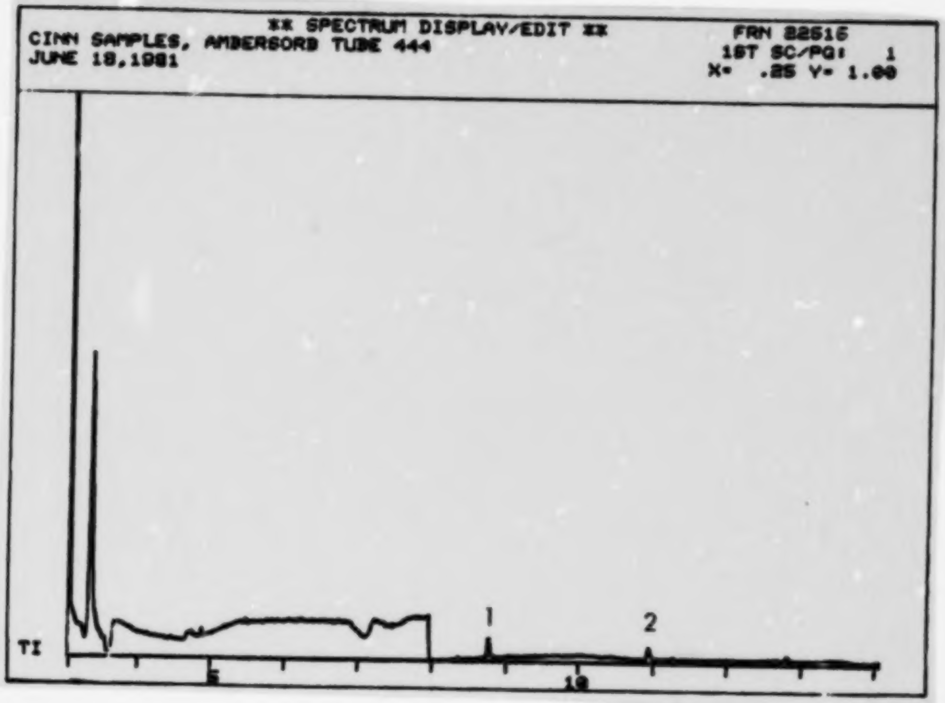

Figure 42. Reconstructed total ion chromatogram of First Ambersorb collector contents, Cincinnati Sampling.

TABLE 56. COMPOUNDS DETECTED IN SECOND AND THIRD SORBENT TUBES DURING SAMPLING IN CINCINNATI

Peak number[a]	Compound
Porapak Collector - second in series	
1	Methylcyclopentane
2	Benzene
3	2-Methylhexane
4	Trimethylpentane
5	C_7-Paraffin
6	n-Heptane
7	Methylcyclohexane
8	Methylheptene
9	Toluene
10	2-Methylheptane
11	3-Methylheptane
12	Tetrachloroethylene
13	Octane
14	Ethylbenzene
15	Xylenes
16	Xylene
17	C_9-Paraffin
Ambersorb Collector - third in series	
1	Benzene
2	Toluene

[a] Refers to peak number in chromatogram presented in Figures 41 and 42.

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APPENDIX A

OPERATION MANUAL

PURPOSE

The purpose of this manual is to provide the information necessary to construct, prepare, calibrate, and operate the portable miniature collection system which was designed, under EPA contract 68-02-2774, to collect and concentrate a wide variety of atmospheric pollutants from ambient air for later analytical assessment of certain selected organic compounds.

PREPARATION, CLEANING, AND CONDITIONING OF REPLACEABLE SORBENT CARTRIDGES

The portable miniature collection system is comprised of two major parts: the sorbent tube tray, which contains replaceable sorbent cartridges that collect and concentrate organic vapors from an air stream passing through them; and the small personal pump, a DuPont P4000 or Spectrex PAS3000, which draws the air stream through the sorbent tube tray. This section will provide the procedures for preparing the replaceable sorbent cartridges for use in field sampling, while other aspects of preparing, calibrating, and operating the portable miniature collection system will be discussed later in this manual.

Cleaning of Sorbent Materials

The replaceable sorbent cartridges used within the portable sampling system's tube tray consist of three types, each type containing a different sorbent material (Tenax-GC, Porapak R, and Ambersorb XE-340). These sorbents are listed in Table A-1 along with other pertinent information. They may be obtained from their manufacturers, or Tenax-GC and Porapak R may be obtained from a chromatography supply distributor (e.g., Supelco, Alltech, Applied Science, etc.).

Generally, all commercial sorbent materials as received from suppliers contain significant levels of background contamination as the result of production, packaging, and/or transportation. To prepare the sorbent materials for cartridge sampling, their backgrounds must be reduced to minimal levels and then maintained at these levels. To start, one can remove most of the initial

TABLE A-1. PERTINENT SORBENT INFORMATION

Information	Sorbent		
	Tenax-GC	Porapak R	Ambersorb XE-340
Mesh size	35/60 mesh	50/80 mesh	?
Manufacturer's temperature limit	350°C	250°C	>350°C
Conditioning temperature	325°C	230°C	325°C
Desorption temperature	300°C	$\leq$200°C	300°C
Desorption time	20-30 min	30-60 min	30-60 min
Physical description	off-white powder	off-white sphere	black, shiny sphere
Amount packed in a cartridge	0.9 to 1.1 g	1.6 to 1.8 g	3.0 to 3.4 g
Chemical composition	2,6-diphenyl-p-phenylene oxide	N-vinyl pyrrolidone	styrene-divinyl benzene
Major thermal decomposition products	alkyl benzenes, styrene, benzene, alkyl phenols	vinyl pyrrolidone, pyrrolidone	styrene, benzene, alkyl benzenes
Solvent incompatability	chlorinated solvents	?	?
Manufacturer address	Enka, Inc. Netherlands	Waters Associates Milford, MA	Rohm & Haas Philadelphia, PA

contamination from the sorbent materials by an extensive solvent cleanup. The procedure for this solvent cleanup is given below:

1) Soxhlet extract sorbent for 16 to 24 hr with distilled-in-glass (high-purity) methanol.

2) Vacuum dry sorbent at 120°C and approximately 1.02×10^5 Pa (30 in Hg) vacuum for 16 to 24 hr.

3) Soxhlet extract sorbent for 16 to 24 hr with distilled-in-glass (high-purity) pentane.

4) Vacuum dry sorbent at 120°C and approximately 1.02×10^5 (30 in Hg) vacuum for 16 to 24 hr.

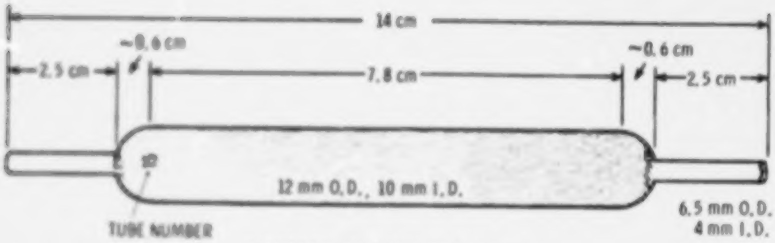
5) Store sorbent in a clean glass jar with a screw-on cap within a dessicator.

At this point the sorbent is clean enough to be loaded into glass cartridge tubes (which will be discussed later), and may be stored for a few months ($\sim$3 to 6 months) without re-extraction as long as it is protected from contaminants. Sorbent may also be stored for several weeks under solvent after one of the extraction procedures and prior to vacuum drying, if desired.

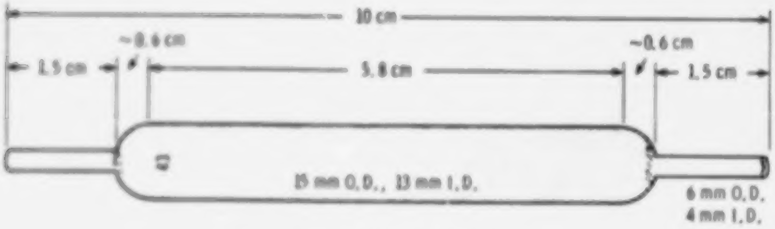
The purpose of this sorbent cleanup procedure is to remove most contaminants from the sorbent material; however, contaminants may also be added during this cleanup procedure, such as from trace impurities present in the solvent, if one is not careful to prevent such contamination. Therefore, one should always use high-purity solvents and clean glassware during soxhlet extractions, and the glass joints should be sealed with Teflon tape or Teflon sleeves (not with silicone grease). Furthermore, a small charcoal trap should be used in the vacuum line of the vacuum oven to prevent the contamination of the drying sorbent material by the back-diffusion of vacuum-pump lubricants.

Preparation of Glass Cartridge Tubes

In addition to cleaning the sorbent materials which are contained within the replaceable sorbent cartridges, the glass cartridge tubes must also be appropriately prepared. The first step of this preparation is to make these tubes (using pyrex glass) according to the one of specifications given in Figure A-1. These tapered cartridge designs have been found to allow an appropriate compromise of sorbent cartridge properties, such that pressure drop is kept to a minimum, thermal desorption and sorbent capacity properties are kept to a maximum, and the sorbent material is adequately contained. The later design (Figure A-1B) provides less pressure drop across a sampling system due to its slightly larger diameter. This design was used in final field evaluations to improve the



A. NARROW - DIAMETER TUBE DESIGN



B. LARGE - DIAMETER TUBE DESIGN.

Figure A-1. Specifications of selected sampling tube design.

performance of the portable miniature collection system. During the manufacture of these glass cartridge tubes, each tube should be numbered (at one end, as indicated in Figure A-1) to permit easy identification of sorbent cartridges for record-keeping and sampling purposes. These numbers should be able to withstand high temperatures (400°C) and should not be washed off by common laboratory solvents (acetone, methanol, toluene, methylene chloride, or pentane). Ceramic numbers annealed to the glass at +400°C have been found to be quite suitable. Preferably, the numbers should be a distinct bright color, such as red, although other colors are permissible as long as they can be distinguished.

Once the glass cartridge tubes have been constructed, they may be stored indefinitely in their empty condition. However, before sorbent is packed within them, the glass tubes should undergo the cleaning and deactivating procedures listed below.

1) Clean glass tubes in a heated ultrasonic bath containing glassware detergent (e.g., Microclean, LiquiNox, etc.) for 4 to 8 hr, or meticulously "hand-clean" with glassware detergent and a soft test tube brush.

2) Rinse interior and exterior with methanol (reagent grade).

3) Bake tubes dry at 300°C to 400°C for 8 to 16 hr.

4) Prepare a 10% solution of dimethyldichlorosilane in high-purity, distilled-in-glass toluene (deactivating solution).

5) Soak glass tubes in deactivating solution for at least 15 min.

6) Thoroughly rinse tubes with high-purity, distilled-in-glass methanol.

7) Bake tubes dry at ~300°C for 8 to 16 hr.

8) Store glass tubes in a clean, dry environment.

While following the procedures just described, care should be taken to avoid contaminating the tubes (with fingerprints, etc.). Therefore, the tubes should always be handled while wearing protective gloves and/or with clean utensils (e.g., tweezers, tongs, etc.). Furthermore, after cleaning and deactivating, the tubes should be packed with the appropriate sorbent material(s) within a reasonable period of time (~ one month).

Cleaning of Other Hardware Materials

The other materials (other than the sorbent materials and glass tubes) which are used in the preparation and storage of the replaceable sorbent cartridges include glass wool, which is used to contain sorbent within the glass cartridges, and stainless steel fittings, viton o-rings, and culture tubes, which are used to seal and store the sorbent cartridges.

Generally, glass wool as received from a chromatography supply distributor (e.g., Supelco, Alltech, Applied Science, etc.) should be clean enough for packing the sorbent cartridges since little of this material is used and the sorbent cartridges are conditioned after packing. The type of glass wool ordered should be a soft, fine pyrex wool which has been silanized (preferably with dimethyldichlorosilane). If the glass wool which is available is probably contaminated (through use), then either new glass wool should be ordered or the contaminated glass wool should undergo the following procedures.

1) Soxhlet extract glass wool for 16 to 24 hr with high-purity distilled-in-glass methanol.

2) Vacuum dry glass wool at 120°C and approximately 1.02×10^5 Pa (30 in. Hg) vacuum for 16 to 24 hr.

3) Soxhlet extract glass wool for 16 to 24 hr with high-purity distilled-in-glass pentane.

4) Vacuum dry glass wool at 120°C and approximately a 30 in. Hg vacuum for 16 to 24 hr.

5) Prepare a 10% solution (deactivation solution) of dimethyldichlorosilane in high-purity, distilled-in-glass toluene.

6) Soak the glass wool in the above deactivating solution for at least 30 min.

7) Soxhlet extract glass wool for 8 to 16 hr with high-purity, distilled-in-glass methanol.

8) Vacuum dry glass wool at 120°C and approximately 1.02×10^5 Pa (30 in. Hg) vacuum for 24 to 48 hr.

As previously discussed during the cleaning of the sorbent materials, the extraction glassware should be clean; Teflon tape or Teflon sleeves should be used at the glass joints instead of silicone grease; and a charcoal trap should be used in the vacuum line of the vacuum oven to prevent contamination of the glass wool by the back-diffusion of vacuum-pump lubricants. This procedure, however, has been found to create a problem with silicon contamination due to excess slianizing reagent retained on the glass wool. Blank analyses of glass wool, therefore, should be performed to determine whether it is suitable for packing sorbent tubes. If unacceptable, the extraction and drying procedures should be repeated.

After the glass cartridges are packed with the sorbent materials (which will be discussed later), the sorbent cartridges are sealed with stainless steel fittings and viton o-rings, and placed within pyrex culture tubes (200 mm long by 25 mm diameter) with Teflon-lined, screw-on caps for storage (as depicted in Figure A-2). Since these materials are to be used to protect the sorbent cartridges from atmospheric contaminants, they should be prepared in such a manner that they introduce minimal contaminants to the sorbent cartridges. To do so, the viton o-rings, stainless steel fittings, pyrex culture tubes, and the Teflon-lined, screw-on culture tube caps should be cleaned according to the procedures listed below.

1) Clean indicated items in a heated ultrasonic bath containing glassware detergent (e.g., Microclean, LiquiNox, etc.) for 4 to 8 hr.

2) Thoroughly rinse these materials with high-purity, distilled-in-glass methanol.

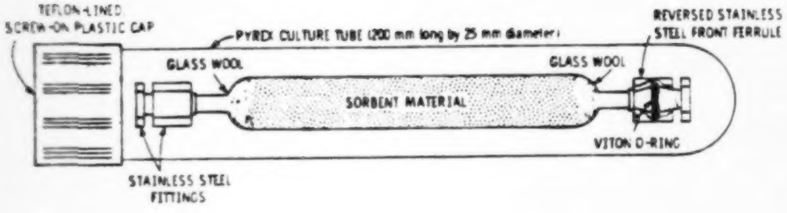

TEFLON-LINED
SCREW-ON PLASTIC CAP
PYREX CULTURE TUBE (200 mm long by 25 mm diameter)
REVERSED STAINLESS
STEEL FRONT FERRULE
GLASS WOOL
GLASS WOOL
SORBENT MATERIAL
VITON O-RING
STAINLESS STEEL
FITTINGS

Figure A-2. Materials used to seal and store a sorbent cartridge.

3) Bake items dry at ~120°C for 8 to 16 hr.

4) Store items in a clean, dry environment until used.

Preparation of Sorbent Cartridges

With the sorbent materials solvent cleaned and dried, the glass cartridge tubes cleaned and deactivated; and the other hardware materials (glass wool, stainless steel fittings, etc.) cleaned; all the required materials are ready for the sorbent cartridges to be prepared for sampling. This preparation consists of two major steps: (1) packing the sorbent tubes and (2) thermally conditioning them to remove most remaining contaminants, thereby reducing their backgrounds to minimal levels.

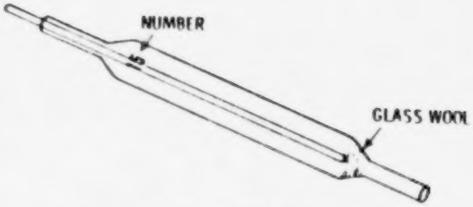
To pack a sorbent cartridge the procedures given below should be followed, with all weights carefully recorded (this will be discussed more thoroughly later).

1) Weigh an empty glass cartridge tube.

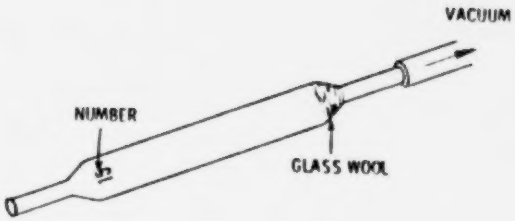
2) Weigh two small pieces of glass wool (~10 to 20 mg each).

3) Place one piece of glass wool into the glass cartridge tube at one of the tapered ends just before the 6 mm O.D. portion of the tube (see Figure A-3A).

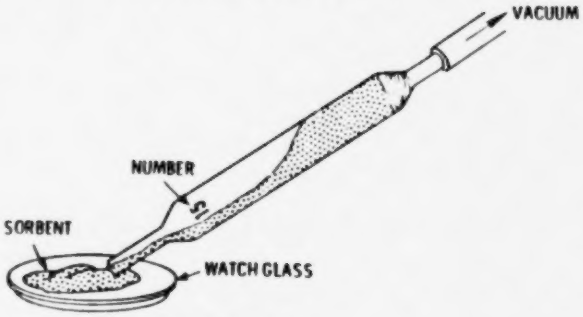
4) Draw a vacuum at this end of the sorbent tube (see Figure A-3B).


NUMBER
GLASS WOOL

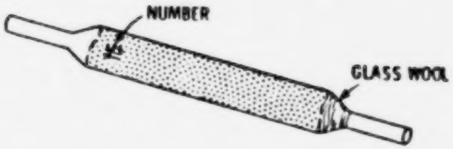
A. PLACE GLASS WOOL AT ONE TAPERED END.


VACUUM
NUMBER
GLASS WOOL

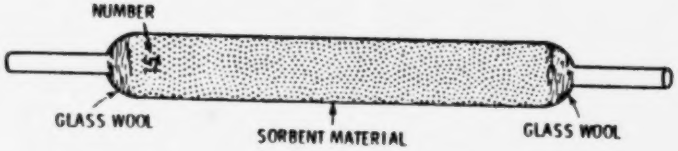
B. ATTACH TUBE TO A VACUUM.


VACUUM
NUMBER
SORBENT
WATCH GLASS

C. "VACUUM" SORBENT INTO TUBE.


NUMBER
GLASS WOOL

D. LEAVE ROOM FOR OTHER GLASS WOOL PLUG.


NUMBER
GLASS WOOL
SORBENT MATERIAL
GLASS WOOL

E. PLACE REMAINING GLASS WOOL AT UNPLUGGED TAPERED END.

Figure A-3. Procedure for packing a sorbent cartridge.

5) Place several grams of one of the three sorbent materials in a clean, shallow, glass container (e.g., watch glass, petri dish, etc.).

6) "Vacuum" the sorbent material into the glass cartridge tube until just a small space is left at the unplugged tapered end just before the 6 mm O.D. portion of the tube (see Figure A-3C and A-3D).

7) Remove the vacuum and place the remaining piece of glass wool at the other end of the tube (see Figure A-3E).

8) Weigh the sorbent cartridge and determine the amount of sorbent within the cartridge.

9) Modify the amount of sorbent placed within the cartridges to try to attain the sorbent quantities specified in Table A-1 (0.9 to 1.1 g of Tenax-GC, 1.6 to 1.8 g of Porapak R, and 3.0 to 3.4 g of Ambersorb XE-340).

While packing the sorbent cartridges as just described, care should be taken to avoid extraneous contamination of the sorbent materials, glass wool, or glass cartridge tubes. Therefore, as previously indicated, all materials should be handled while wearing protective gloves and/or with clean utensils (e.g., tweezers, tongs, etc.). The vacuum line should include a charcoal trap to prevent contamination by the back-diffusion of pump lubricants. Generally, these procedures may be followed in the open laboratory. Although, the sorbent will quickly adsorb vapors present in the lab air, the thermal conditioning procedure should remove these contaminants. However, if a clean-box or clean-room is available, then these facilities would be preferred while packing the sorbents since a clean, inert atmosphere would further reduce potential background and contamination.

After the sorbent cartridges have been packed, they need to be thermally conditioned to remove most remaining contaminants thereby reducing their backgrounds to minimal levels and making them suitably clean for sampling. The current techniques which are used to condition sorbent cartridges have been found to be adequate for most sampling applications.

The sorbent cartridge thermal conditioning technique is straightforward and simply involves passing a purified, inert stream of gas (helium or nitrogen) at ~30 mL/min through a sorbent cartridge for 16 to 24 hr with the sorbent cartridge heated to an appropriate temperature (230°C for Porapak R, and 325°C for Tenax-GC and Ambersorb XE-340). The gas stream should be purified by placing a drierite trap, a molecular sieve trap, and a charcoal trap in the gas stream (in that order) before passing the gas stream through the sorbent cartridges.

One technique of thermal conditioning is to attach the gas stream to a manifold comprised of stainless steel fittings and contained within a laboratory oven (with a maximum temperature of $\geq$325°C). A small section of such a manifold is sketched in Figure A-4, shown with a few sorbent cartridges attached. A manifold of this type can be extended to condition as many tubes as there is room for within the laboratory oven, as long as a flow rate of ~30 mL/min can be attained through the tubes. The tubes are connected to the manifold using graphite ferrules.

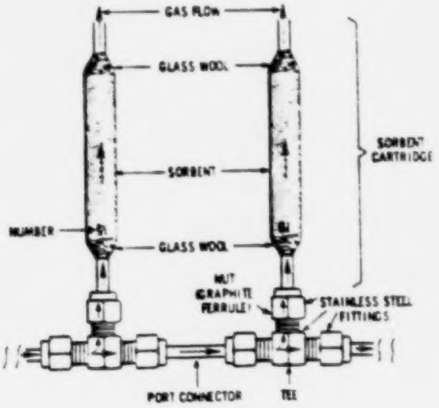


Figure A-4. Section of manifold used for thermally conditioning sorbent cartridges.

The critical portion of this sorbent cartridge thermal conditioning technique occurs after the cartridges have been purged with purified gas in a heated environment and are ready to be removed from the conditioning manifold to be stored for later sampling. As mentioned previously, sorbent will quickly adsorb vapors present in the lab air. This will occur as soon as thermal conditioning is stopped (i.e., heat and purge gas are turned off). Therefore, it is imperative that the sorbent cartridges be sealed from contaminating laboratory atmosphere as soon as possible after thermal conditioning is discontinued. When the sorbent cartridges are barely cool enough to be handled (while wearing protective gloves and/or using clean utensils), the nuts (with graphite ferrules) which are used to connect the cartridges to the manifold should be carefully (the cartridges easily break while hot) loosened. As rapidly as possible the sorbent cartridges should then be removed by slipping them out of the manifold nuts and then sealed with metal fittings and o-rings (as shown previously in Figure A-2). After all the sorbent cartridges are sealed in this manner, they should be placed inside individual culture tubes and the culture tubes sealed with their Teflon-lined, screw-on plastic caps (see Figure A-2). These sorbent tubes are now properly prepared for collecting samples.

Another technique of thermal conditioning was devised in an attempt to resolve the problem of sorbent tube contamination with laboratory air between thermal conditioning and sealing of the sorbent tubes. This technique uses a Nutech Model 322-14X2 Cartridge Conditioning System for thermal conditioning of the sorbent cartridges. The Nutech Thermal Desorption System is comprised of an electrically heated metal block containing fourteen, Teflon-sealed, cylindrical chambers; a system of drilled holes and metal tubing for carrier gas flow through the conditioning chambers; and, an electronic temperature controlling/monitoring unit. This system, depicted in Figure A-5, is contained within a Labcono Model 50004 Controlled Amosphere Glove Box which is used as a "clean" box. The gas supplies to the desorption system and glove box are both purified with appropriate traps.

Larger-diameter sorbent tubes (Figure A-1B) are thermally conditioned by dropping them into the conditioning chambers, sealing the chambers with the Teflon seals, passing purfied gas through the sorbent tubes, and heating the Nutech system to an appropriate temperature. The glove box is slowly purged with purified nitrogen thoughout and after thermal conditioning. When thermal conditioning is complete, the Nutech system is slowly cooled, the gas flow to the Nutech system is shut-off, and the sorbent tubes are removed from the Nutech system and capped within the glove box as soon as they are cool enough to handle. Since the sorbent tubes are within a "clean" environment when they are sealed, contamination with organics in the laboratory atmosphere doesn't occur. Although this technique provides thermally conditioned sorbent tubes with minimal background, the handling of the sorbent tubes within a glove box is very awkward. The previous technique also generally provides thermally conditioned sorbent tubes with acceptable background levels.

To assure the sorbent backgrounds are at their minimal levels, sampling should be done as soon as possible after the tubes are conditioned (preferably ≤ one week). Tubes stored for more than ~one week should again be thermally conditioned prior to sampling. Any labels which are used to designate the samples the sorbent cartridges are to be used to collect (or blanks, etc.) should be affixed to the outside of the culture tube to prevent the ink or adhesive from contaminating the sorbent. Finally, if rough handling is anticipated, especially during transportation, clean glass wool should be placed within the culture tube surrounding the sorbent cartridge to offer the cartridge additional cushioning and protection from breakage.

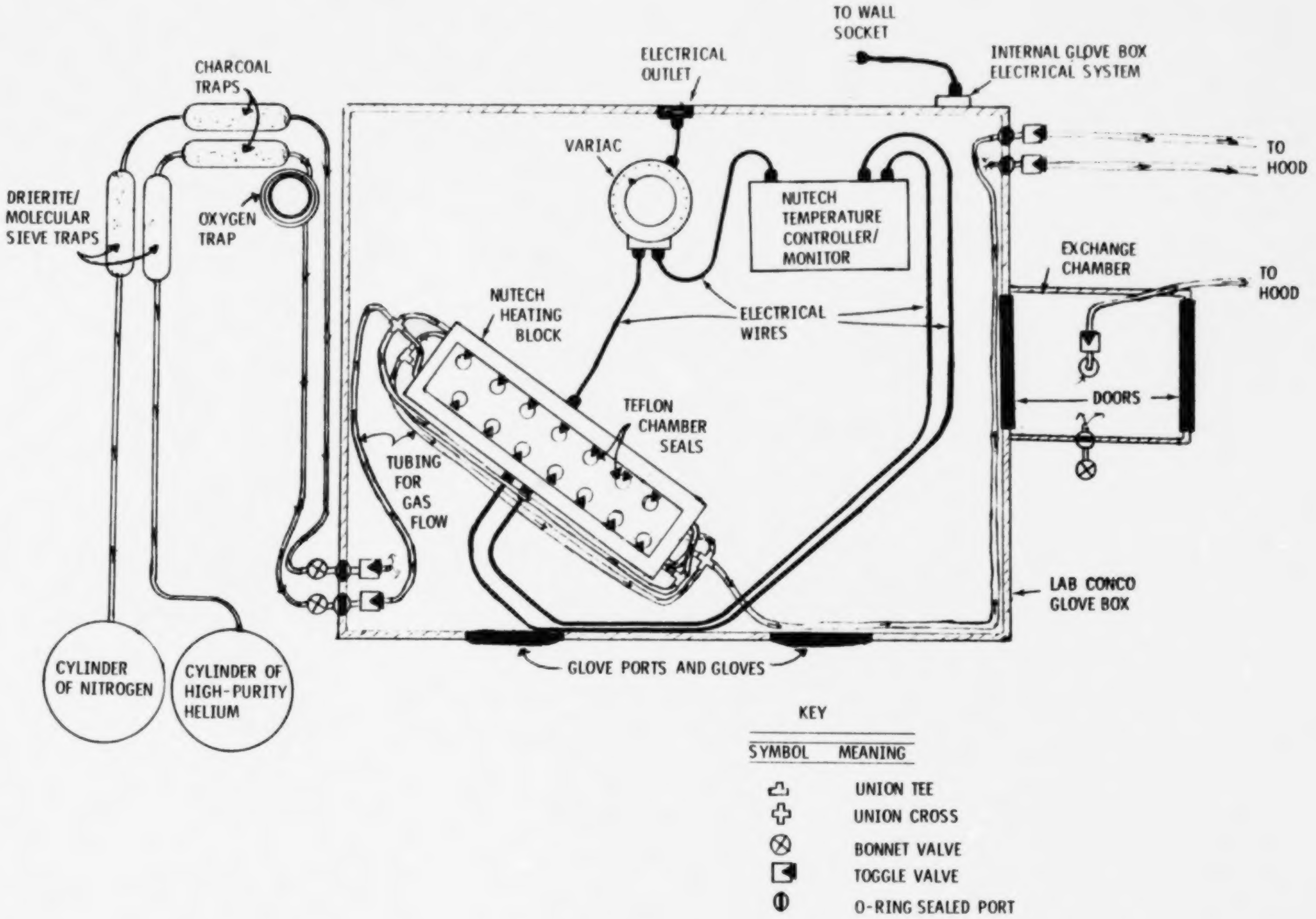

TO WALL SOCKET
ELECTRICAL OUTLET
INTERNAL GLOVE BOX ELECTRICAL SYSTEM
CHARCOAL TRAPS
DRIERITE/ MOLECULAR SIEVE TRAPS
OXYGEN TRAP
VARIAC
NUTECH TEMPERATURE CONTROLLER/ MONITOR
TO HOOD
EXCHANGE CHAMBER
TO HOOD
NUTECH HEATING BLOCK
ELECTRICAL WIRES
TEFLON CHAMBER SEALS
TUBING FOR GAS FLOW
DOORS
LAB CONCO GLOVE BOX
CYLINDER OF NITROGEN
CYLINDER OF HIGH-PURITY HELIUM
GLOVE PORTS AND GLOVES
KEY
SYMBOL
MEANING
UNION TEE
UNION CROSS
BONNET VALVE
TOGGLE VALVE
O-RING SEALED PORT

Figure A-5. System for thermally desorbing sorbent cartidges within "clean" glove box.

Storage, Background, and Contamination

As mentioned several times previously, precautions should be taken to prevent contamination of a sorbent cartridge during its preparation. These precautions include handling all materials while wearing protective gloves and/or using clean utensils, using high-purity, distilled-in-glass solvents, using Teflon-tape or Teflon-sleeves instead of silicone grease at soxhlet extractor glass joints, placing a charcoal trap in the vacuum line of a vacuum oven system to prevent the contamination of drying materials by the back-diffusion of pump lubricants, and many others (which have been previously stated). The purpose of cleaning the sorbent and other materials, taking precautions to prevent contamination during sorbent cartridge preparation, and conditioning the sorbent cartridges within ∿one week of sample collection is to assure that the sorbent cartridges have minimal levels of background and contamination.

It should be noted here, however, that although contamination can contribute to the background (materials present during a sorbent cartridge analysis when no materials have been added to the cartridge [i.e., a blank]) present on a sorbent cartridge, background can also be contributed by the sorbent material through slow degradation (or "aging"). For this reason a sorbent cartridge should be reconditioned just prior to sampling if it has been stored for more than ∿one week. However, the thermal or chemical decomposition of a sorbent caused by sampling/analytical conditions also can significantly contribute to sorbent cartridge backgrounds. Thermal decomposition of a sorbent results, of course, from overheating the sorbent cartridge during conditioning, sampling, or desorption. Therefore, not exposing the sorbent cartridges to temperatures above their temperature limits (given in Table A-1) should minimize thermal decomposition problems. Chemical decomposition caused by exposing the sorbent cartridges to inappropriate solvents (also given in Table A-1) should also be avoided. Chemical decomposition may also be caused by reactive species (such as NO_x, SO_2, and HCl) in the sample matrix (which if anticipated can be potentially removed by selective filters placed prior to the sorbent cartridge), but they should not present a major problem with ambient air samples.

Usually, the analyses of "blank" sorbent cartridges is enough to indicate the type of compounds and their levels which comprise the sorbent background. Quite often, background (of a particular sorbent) from many "blank" tubes vary somewhat in their amounts, as indicated by peak sizes (or areas), but retain a certain pattern (i.e., peaks from various analyses have similar retention times and similar chemical type). This pattern is probably due to compounds produced by sorbent decomposition which is typical for that particular sorbent because of the chemical composition of the sorbent. For example, Table A-1 lists some of the major thermal decomposition products that might be expected for the sorbent materials used for this project based on their chemical composition (also given in Table A-1). Knowing the types of decomposition products to expect from a particular sorbent, one can determine whether thermal or chemical decomposition of the sorbent likely occurred during sample collection, such as from matrix effects. Therefore, one can evaluate whether the compounds detected during an analysis of a sorbent cartridge sample are the result of the collected sample or some type of sorbent decomposition.

Records

It was briefly noted when discussing the packing of the sorbent cartridges that records should be kept of all glass cartridge tube and sorbent weights. Indeed, the reason that numbers are to be permanently annealed to the glass cartridge tubes is for record-keeping purposes. It is essential that accurate histories be kept for each sorbent tube in order to assure the quality control of all sorbent cartridge samples. Therefore, the sorbent cartridges must be marked in some manner (the annealed numbers) in order to assure individual identification. Furthermore, all manipulations of the sorbent cartridge or the sorbent material, including weights, cleanup and conditioning procedures, and storage times, need to be recorded and associated with each sorbent cartridge. By keeping such accurate histories of each sorbent cartridge, one avoids such poor quality control situations as trying to compare the results of two duplicate samples, one collected on a freshly packed sorbent cartridge and the other collected on a sorbent cartridge in use for at least five years. Obviously, a great disparity of results could be caused by the difference in "age" and treatment of the two sorbent cartridges. In addition, such recordkeeping helps to prevent the possibility of getting different types (i.e., packed with different sorbent materials) of sorbent cartridges mixed-up and overheating some during conditioning because the wrong thermal conditioning temperature was used. For example, if a few Porapak R sorbent cartridges are conditioned with a number of Tenax-GC sorbent cartridges at the conditioning temperature of Tenax-GC (325°C), the temperature limit of the Porapak R sorbent cartridges (250°C) would be exceeded and the Porapak R would thermally decompose. Therefore, the history of each sorbent tube should be kept meticulously, beginning with the "initiation" of the sorbent cartridge, which should include sorbent cleanup procedures, sorbent cartridge weights, and conditioning information; continuing through the sorbent cartridge's "sampling lifetime," which should include storage, packaging, and transportation information, sampling conditions and dates, and analytical log-in numbers, procedures, and results; and ending with the "termination" of the sorbent cartridge, which should include the procedure and date the cartridge was either reconditioned or unpacked. All of this information should be kept on each sorbent cartridge according to its annealed number and retained within a sorbent history log book. Figure A-6 depicts the information which should be kept within the log book associated with the "initiation" of each sorbent cartridge, information which should be entered while following the procedure in this section of this Operation Manual. The records associated with the aspects of a sorbent cartridge's "sampling lifetime" and "termination" will be further discussed later in this manual.

FLOW CHART

For convenience, a flow chart which summarizes the procedures for the preparation, cleaning, and conditioning of the replaceable sorbent cartridges is given in Figure A-7.

PREPARATION, CALIBRATION, AND OPERATION OF THE PORTABLE MINIATURE COLLECTION SYSTEM

This section of this manual describes the preparation, operation, and calibration of the portable miniature collection system. Included are instructions on how to assemble the replaceable sorbent cartridges within a sorbent tube tray, how to calibrate the portable miniature collection system with a sorbent tube tray attached, and how to set up and monitor this sampling system. In addition, quality control, storage, recordkeeping, and other aspects of a field sampling program are discussed. This section should provide enough information for the collection of ambient air samples using replaceable sorbent cartridges and small personal pumps, and the handling of these samples until analysis.

Design and Preparation of the Sorbent Tube Tray

This part of this manual describes the preparation of the sorbent tube tray which is used to contain the replaceable sorbent cartridges that collect and concentrate organic vapors from an air stream passing through them. The preparation, cleaning, and conditioning of these replaceable sorbent cartridges was described in the previous section of this manual. At the end of that section, the sorbent tubes, consisting of three types (Tenax-GC, Porapak R, and Ambersorb XE-340), were ready to be used for sample collection. Through cleaning and conditioning their background levels had been reduced to a minimum and this minimal background level maintained by storing the tubes capped with metal fittings and o-rings inside a culture tube with a Teflon-lined screw-top cap. The hardware needed for the storage of each sorbent tube is described in Table A-2 and the use of these materials for tube storage is demonstrated by Figure A-8. For sample collection, four sorbent tubes of specific types will be connected in series within a special tray, such that the collected air sample first passes through a Tenax sorbent tube,

Name:

Tube #: Sorbent Type: Date Packed:

Weight of: Glass Cartridge: Glass Wool: Sorbent:

Sorbent Material Information

Supplier: Mesh Size: Lot #:

Date Opened: Date Arrived: Generation: 1 2 3

Cleanup Procedure:

Cleanup Dates:

Sieve Size: Sieve Date:

Storage Procedures and Conditions:

Storage Dates:

Storage Procedures and Conditions:

Storage Dates:

Sorbent Cartridge Conditioning

Date Packed: Storage Procedure & Dates:

Conditioning Procedure:

Conditioning Date:

Conditioning Procedure:

Conditioning Date:

Conditioning Procedure:

Conditioning Date:

Conditioning Procedure:

Conditioning Date:

Figure A-6. Information which should be recorded in the sorbent cartridge logbook.

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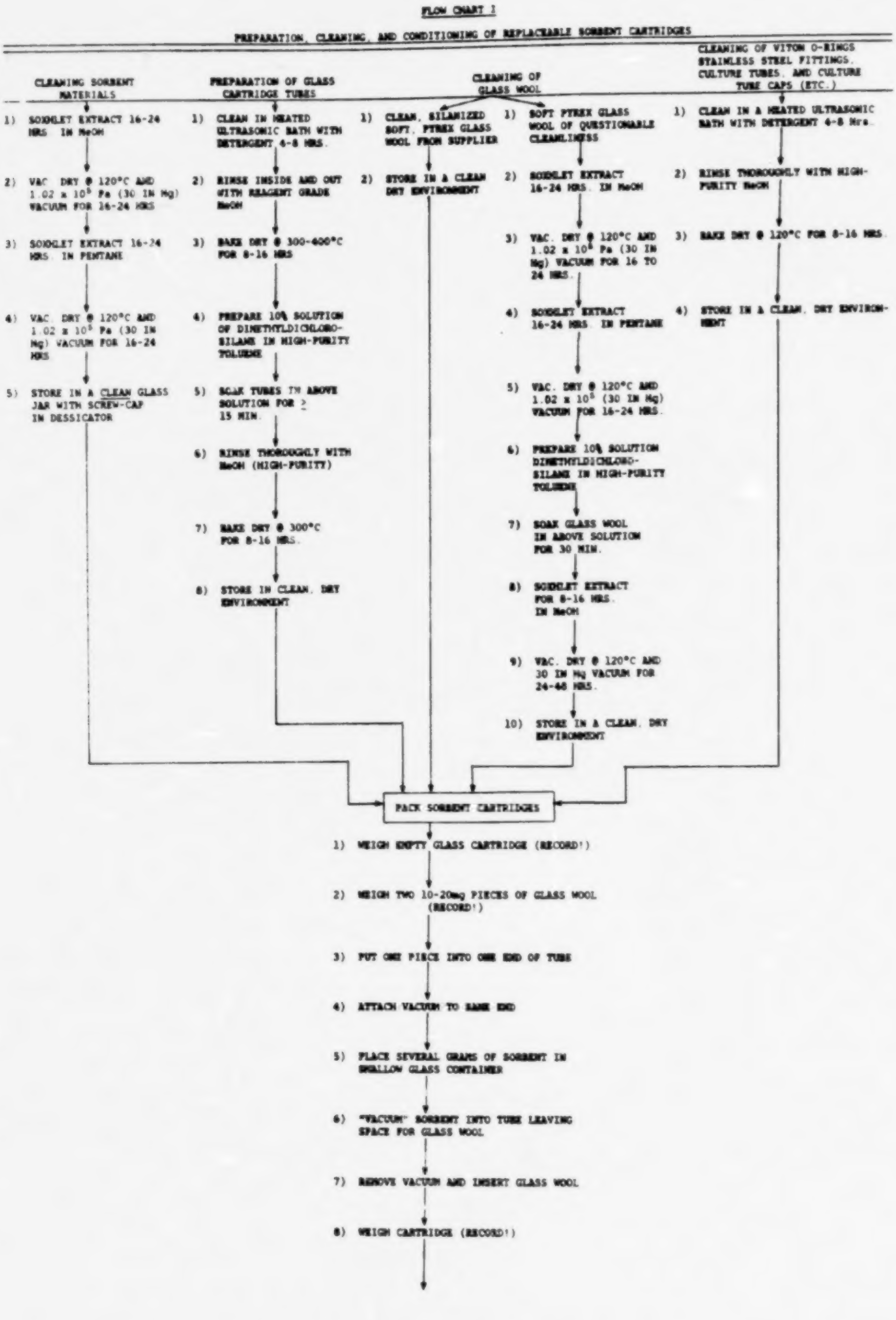

FLOW CHART I
PREPARATION, CLEANING, AND CONDITIONING OF REPLACEABLE SORBENT CARTRIDGES
CLEANING SORBENT MATERIALS
1) SOXHLET EXTRACT 16-24 HRS IN MeOH
2) VAC. DRY @ 120°C AND 1.02 x 10^5 Pa (30 IN Hg) VACUUM FOR 16-24 HRS
3) SOXHLET EXTRACT 16-24 HRS. IN PENTANE
4) VAC. DRY @ 120°C AND 1.02 x 10^5 Pa (30 IN Hg) VACUUM FOR 16-24 HRS
5) STORE IN A CLEAN GLASS JAR WITH SCREW-CAP IN DESSICATOR
PREPARATION OF GLASS CARTRIDGE TUBES
1) CLEAN IN HEATED ULTRASONIC BATH WITH DETERGENT 4-8 HRS.
2) RINSE INSIDE AND OUT WITH REAGENT GRADE MeOH
3) BAKE DRY @ 300-400°C FOR 8-16 HRS
4) PREPARE 10% SOLUTION OF DIMETHYLDICHLORO-SILANE IN HIGH-PURITY TOLUENE
5) SOAK TUBES IN ABOVE SOLUTION FOR ≥ 15 MIN.
6) RINSE THOROUGHLY WITH MeOH (HIGH-PURITY)
7) BAKE DRY @ 300°C FOR 8-16 HRS.
8) STORE IN CLEAN, DRY ENVIRONMENT
CLEANING OF GLASS WOOL
1) CLEAN, SILANIZED SOFT, PYREX GLASS WOOL FROM SUPPLIER
2) STORE IN A CLEAN DRY ENVIRONMENT
1) SOFT PYREX GLASS WOOL OF QUESTIONABLE CLEANLINESS
2) SOXHLET EXTRACT 16-24 HRS. IN MeOH
3) VAC. DRY @ 120°C AND 1.02 x 10^5 Pa (30 IN Hg) VACUUM FOR 16 TO 24 HRS.
4) SOXHLET EXTRACT 16-24 HRS. IN PENTANE
5) VAC. DRY @ 120°C AND 1.02 x 10^5 (30 IN Hg) VACUUM FOR 16-24 HRS.
6) PREPARE 10% SOLUTION DIMETHYLDICHLORO-SILANE IN HIGH-PURITY TOLUENE
7) SOAK GLASS WOOL IN ABOVE SOLUTION FOR 30 MIN.
8) SOXHLET EXTRACT FOR 8-16 HRS. IN MeOH
9) VAC. DRY @ 120°C AND 30 IN Hg VACUUM FOR 24-48 HRS.
10) STORE IN A CLEAN, DRY ENVIRONMENT
CLEANING OF VITON O-RINGS STAINLESS STEEL FITTINGS, CULTURE TUBES, AND CULTURE TUBE CAPS (ETC.)
1) CLEAN IN A HEATED ULTRASONIC BATH WITH DETERGENT 4-8 Hrs.
2) RINSE THOROUGHLY WITH HIGH-PURITY MeOH
3) BAKE DRY @ 120°C FOR 8-16 HRS.
4) STORE IN A CLEAN, DRY ENVIRONMENT
PACK SORBENT CARTRIDGES
1) WEIGH EMPTY GLASS CARTRIDGE (RECORD!)
2) WEIGH TWO 10-20mg PIECES OF GLASS WOOL (RECORD!)
3) PUT ONE PIECE INTO ONE END OF TUBE
4) ATTACH VACUUM TO SAME END
5) PLACE SEVERAL GRAMS OF SORBENT IN SHALLOW GLASS CONTAINER
6) "VACUUM" SORBENT INTO TUBE LEAVING SPACE FOR GLASS WOOL
7) REMOVE VACUUM AND INSERT GLASS WOOL
8) WEIGH CARTRIDGE (RECORD!)

Figure A-7. Flow chart summarizing sorbent cartridge preparation procedures.

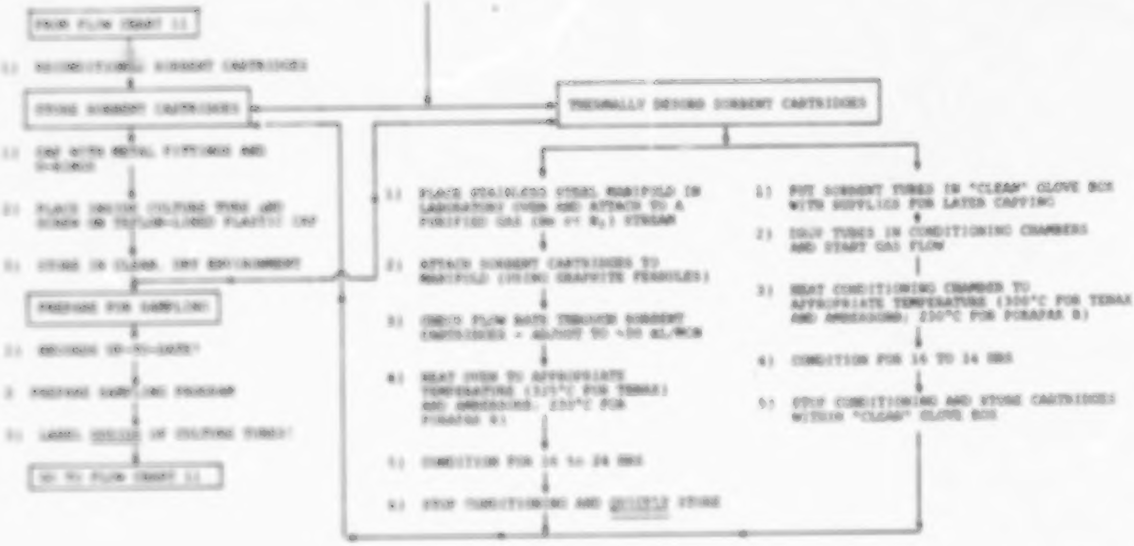

FROM FLOW CHART 11
1) RECONDITIONED SORBENT CARTRIDGES
STORE SORBENT CARTRIDGES
1) CAP WITH METAL FITTINGS AND O-RINGS
2) PLACE INSIDE CULTURE TUBE AND SCREW ON TEFLON-LINED PLASTIC CAP
3) STORE IN CLEAN, DRY ENVIRONMENT
PREPARE FOR SAMPLING
1) RECORDS UP-TO-DATE?
2 PREPARE SAMPLING PROGRAM
3) LABEL OUTSIDE OF CULTURE TUBES?
GO TO FLOW CHART 11
THERMALLY DESORB SORBENT CARTRIDGES
1) PLACE STAINLESS STEEL MANIFOLD IN LABORATORY OVEN AND ATTACH TO A PURIFIED GAS (He or N$_2$) STREAM
2) ATTACH SORBENT CARTRIDGES TO MANIFOLD (USING GRAPHITE FERRULES)
3) CHECK FLOW RATE THROUGH SORBENT CARTRIDGES - ADJUST TO ~30 mL/MIN
4) HEAT OVEN TO APPROPRIATE TEMPERATURE (325°C FOR TENAX AND AMBERSORB; 230°C FOR PORAPAK R)
5) CONDITION FOR 16 to 24 HRS
6) STOP CONDITIONING AND QUICKLY STORE
1) PUT SORBENT TUBES IN "CLEAN" GLOVE BOX WITH SUPPLIES FOR LATER CAPPING
2) [illegible] TUBES IN CONDITIONING CHAMBERS AND START GAS FLOW
3) HEAT CONDITIONING CHAMBER TO APPROPRIATE TEMPERATURE (300°C FOR TENAX AND AMBERSORB; 230°C FOR PORAPAK R)
4) CONDITION FOR 16 TO 24 HRS
5) STOP CONDITIONING AND STORE CARTRIDGES WITHIN "CLEAN" GLOVE BOX

Figure A-7 (continued)

TABLE A-2. HARDWARE MATERIALS REQUIRED FOR STORAGE OF EACH SORBENT TUBE

Item	Material	Size-brand	Quantity
Nut	Stainless steel	6.4 mm (1/4 in.)-Swagelok	Two
Front ferrule	Stainless steel	6.4 mm (1/4 in.)-Swagelok	Two
Cap	Stainless steel	6.4 mm (1/4 in.)-Swagelok	Two
O-ring	Viton	~6.4 mm (~1/4 in.) O.D.	Two
Culture tube	Glass	20 cm long x 2.5 cm diameter-Pyrex, Kimax or equivalent	One
Culture tube screw-top cap	Plastic with teflon liner	For 2.5 cm diameter culture tube	One

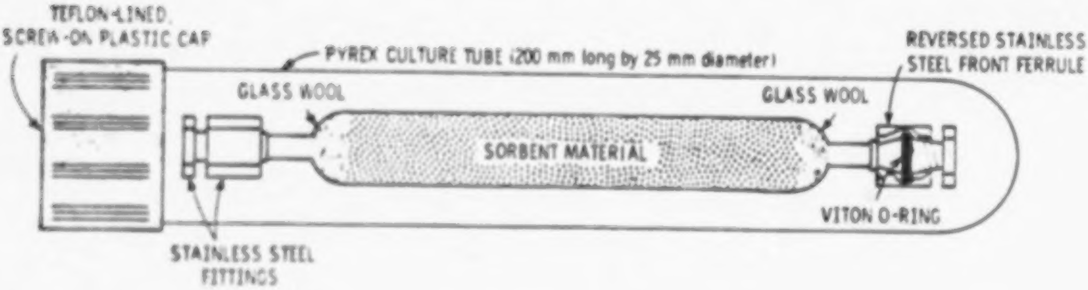

TEFLON-LINED SCREW-ON PLASTIC CAP
PYREX CULTURE TUBE (200 mm long by 25 mm diameter)
REVERSED STAINLESS STEEL FRONT FERRULE
GLASS WOOL
GLASS WOOL
SORBENT MATERIAL
VITON O-RING
STAINLESS STEEL FITTINGS

Figure A-8. Storage of a sorbent tube.

then through a Porapak R sorbent tube, then through an Ambersorb XE-340 sorbent tube, and finally through a second, backup, Ambersorb XE-340 sorbent tube. With these sorbent tubes connected in series in this order, the highest molecular weight compounds will be collected on the Tenax tube, which has the greatest ability of the three sorbents to desorb such compounds. Any intermediate or low molecular weight compounds which "break through" the Tenax tube are then collected by the Porapak R sorbent tube. Very volatile, low molecular weight compounds will "break through" the Porapak R tube also and pass into the first Ambersorb tube which, of the three sorbents, has the greatest ability to retain such compounds. Hopefully, this combination of three tubes will quantitatively collect all compounds of interest to this project, however, some of the very volatile, low molecular weight compounds may "break through" the first Ambersorb tube and pass into the second, backup Ambersorb tube. This backup tube serves to check the ability of the first three tubes to retain the compounds of interest to this project. The quantities of compounds on one or more of the first three sorbent tubes, and not found on the backup tube, should be summed to obtain the total amounts collected. These amounts can then be divided by the sample volume collected to determine the approximate original concentrations of the compounds found in ambient air. For compounds found on the backup sorbent tube as well as one or more of the first three sorbent tubes, their summed quantities should be considered to represent the minimum amounts of these compounds present in the sampled air. When dividing these quantities by the sample volume collected, the concentrations of these compounds in ambient air should be reported as greater than or equal to the values obtained.

In some instances, such as if a number of samples are collected simultaneously, the analysis of one or two Ambersorb backup tubes may suffice to ascertain which, if any, compounds have "broken through". It may then not be necessary or desirable to analyze the rest of the Ambersorb backup tubes collected. Where such a situation is anticipated, using backup tubes with each sample collected may not be desired. Therefore, the backup tubes can be replaced in some of the sorbent tube trays by a piece of stainless steel tubing (6 mm O.D., 10 or 14 mm long). If any question exists about whether or not backup tubes should be used on certain samples, it would probably be advisable to collect the backup samples and later decide whether they should be analyzed.

Figure A-9 gives the dimensions of the aluminum box to be used as a tray for containing the sorbent tubes. It also shows the locations and sizes of holes to be drilled for attaching the tube retaining clips, the tray cover, and the 6.4 mm (1/4 in.) stainless steel bulkhead unions. The rest of the hardware necessary for use within the sorbent tube tray are listed in Table A-3. If the tray is not to be mounted to a pump, then a belt clip or some other means of attaching the tray to a person should be put on the tube tray. For cleaning, the aluminum box and retaining chips should be rinsed with tap water and dried. The rest of the hardware materials for the sorbent tube tray should be prepared according to the procedures given prevously for the cleaning of hardware materials for sorbent tube storage. After cleaning the sorbent tube tray and fittings, three stainless steel/teflon connectors, as depicted in Figure A-10, should be assembled in the laboratory using appropriate care such as by wearing protective gloves to prevent contamination from handling. The stainless steel/teflon connectors should then be placed within the tube tray and the cover placed on the tray to assure that all necessary parts are readily available for the "loading" of this tray with sorbent tubes in the field.

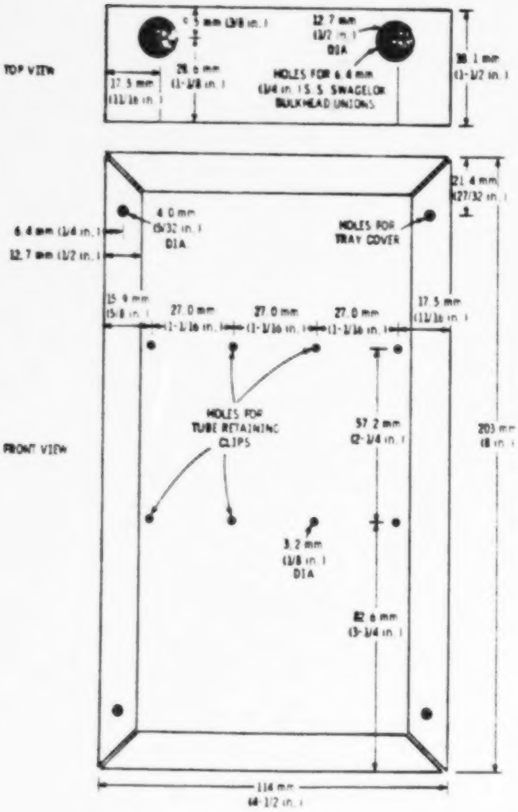

9.5 mm (3/8 in.)
12.7 mm (1/2 in.) DIA
TOP VIEW
17.5 mm (11/16 in.)
28.6 mm (1-1/8 in.)
HOLES FOR 6.4 mm (1/4 in.) S.S. SWAGELOK BULKHEAD UNIONS
38.1 mm (1-1/2 in.)
21.4 mm (27/32 in.)
4.0 mm (5/32 in.) DIA
6.4 mm (1/4 in.)
12.7 mm (1/2 in.)
HOLES FOR TRAY COVER
15.9 mm (5/8 in.)
27.0 mm (1-1/16 in.)
27.0 mm (1-1/16 in.)
27.0 mm (1-1/16 in.)
17.5 mm (11/16 in.)
HOLES FOR TUBE RETAINING CLIPS
57.2 mm (2-1/4 in.)
203 mm (8 in.)
FRONT VIEW
3.2 mm (1/8 in.) DIA
82.6 mm (3-1/4 in.)
114 mm (4-1/2 in.)

Figure A-3 Dimensions of tube tray, and locations and sizes of drilled holes.

TABLE A-3. HARDWARE REQUIREMENTS FOR EACH TUBE TRAY

Item	Material	Size (brand)	Quantity
Tray with cover	Aluminum	20 cm (8 in.) x 11 cm x (4 1/2 in.) x 4 cm (1 1/2 in.)	One
Bulkhead union	Stainless steel	6.4 mm (1/4 in.)-Swagelok	Two
Reducing union	Stainless steel	6.4 mm (1/4 in.) to 3.2 mm (1/8" in.)-Swagelok	Six
Nut	Stainless steel	3.2 mm (1/8 in.)-Swagelok	Six
Front ferrule	Stainless steel	3.2 mm (1/8 in.)-Swagelok	Six
Back ferrule	Stainless steel	3.2 mm (1/8 in.)-Swagelok	Six
Plug	Stainless steel	6.4 mm (1/4 in.)-Swagelok	Ten
Tubing	Teflon	57 mm (2 1/4 in.) to 64 mm (2 1/2 in.) long, 5.1 mm (1/5 in.) O.D., 1.6 mm (1/16 in.) I.D.	Three
Clips	(Metal)	- for 12 mm O.D. tubes	Eight
Screws	(Metal)	- for tray cover - for retaining clips	Four Eight

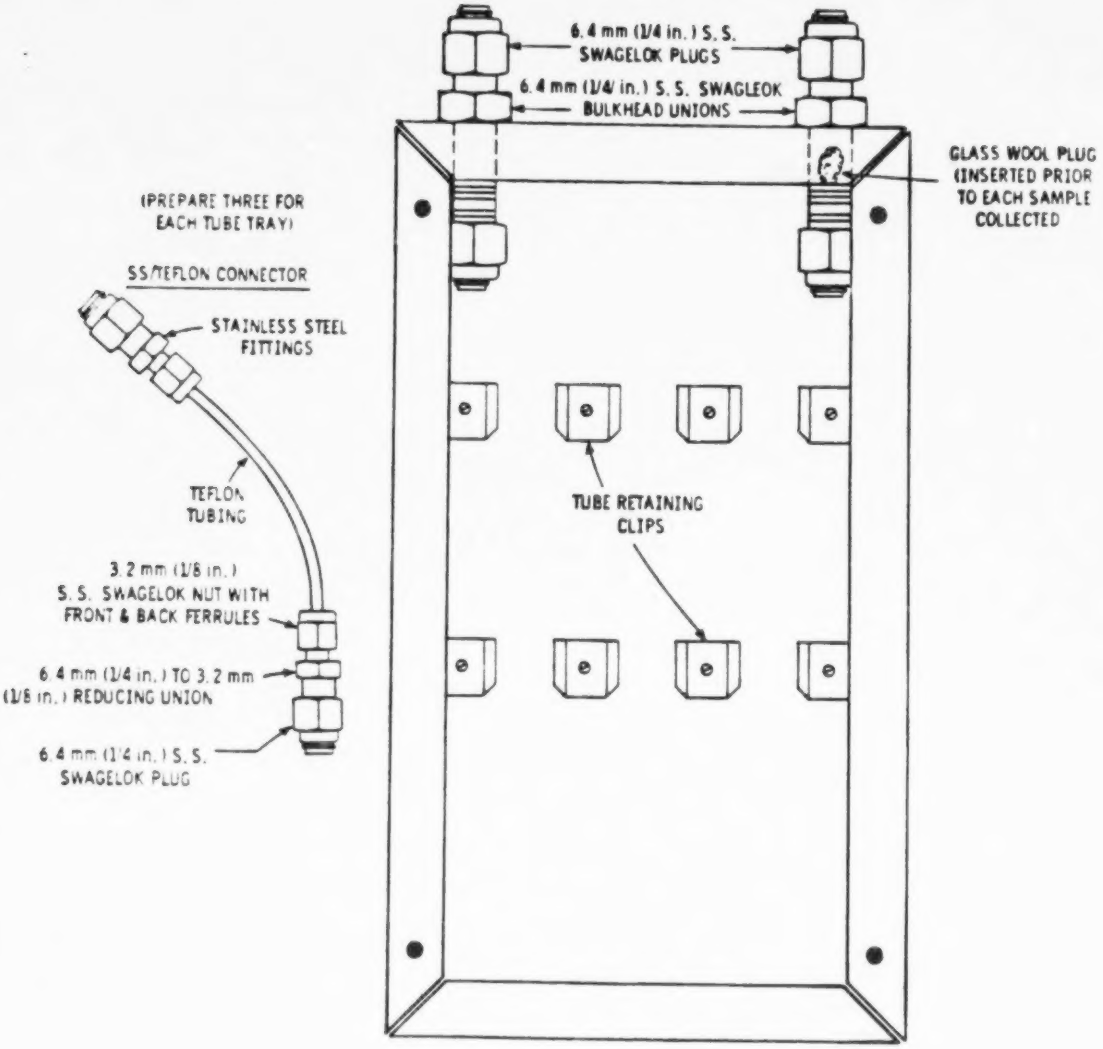

6.4 mm (1/4 in.) S. S. SWAGELOK PLUGS
6.4 mm (1/4 in.) S. S. SWAGLEOK BULKHEAD UNIONS
GLASS WOOL PLUG (INSERTED PRIOR TO EACH SAMPLE COLLECTED
(PREPARE THREE FOR EACH TUBE TRAY)
SS/TEFLON CONNECTOR
STAINLESS STEEL FITTINGS
TEFLON TUBING
TUBE RETAINING CLIPS
3.2 mm (1/8 in.) S. S. SWAGELOK NUT WITH FRONT & BACK FERRULES
6.4 mm (1/4 in.) TO 3.2 mm (1/8 in.) REDUCING UNION
6.4 mm (1/4 in.) S. S. SWAGELOK PLUG

Figure A-10. Tube tray with all hardware assembled.

Step by step instructions for the "loading" of the tube tray with four sorbent tubes are given in Figures A-11 through A-22. It should be remembered that sorbent tubes quickly adsorb vapors from the atmosphere when they are opened, which introduces an error to the quantitation of compounds collected. Therefore, the tubes should be assembled quickly and, as shown by the figures, caps and plugs should remain in position until a connection is to be made at that position. Furthermore, once a connection is made, it should immediately be tightened with wrenches to assure a good seal. To prevent the introduction of contamination from handling the sorbent tubes, they should be assembled while wearing protective latex gloves. In addition, the ends of the sorbent tubes (i.e., at the metal fittings) should not be touched or otherwise disturbed, because these ends will later be exposed to the analytical system during sorbent tube desorption. After the sorbent tube tray is "loaded", it is ready to be connected to a small personal pump for sample collection. Since the sorbent tubes are not as well protected from contamination within the tube tray as they are when stored, a sample should be collected with the tube tray within a few hours after being loaded.

Operation of the Small Personal Pump

Two types of small personal pumps, DuPont Model P4000 and Spectrex Model PAS-3000, have been used in the portable miniature collection system. The DuPont pump was originally selected for use in this system, because it had the best flow rate capabilities over a substantial pressure drop of personal pumps commercially available at that time (when it was chosen). However, during field evaluations of the portable miniature collection system, there was difficulty maintaining the capabilities of the DuPont pumps and keeping them operating properly. This durability problem was attributed to the operation of these pumps at the extremes of their flow rate/pressure drop specifications. Therefore, the Spectrex pump, a newer type of personal pump with somewhat better flow rate/pressure drop capabilities, was selected as an alternative to the DuPont pump. In the field the Spectrex pump was better able to achieve and maintain a 1 L/min flow rate through a portable miniature collection system than a DuPont pump. Other personal pumps may also be used in the portable miniature collection system as long as their flow rate/pressure drop capabilities are at least as good as the specifications for the DuPont pump [1 L/min at Pa(25 in H_2O)].

The operation of different types of small personal pumps vary significantly. Furthermore, different pumps may have various accessories, such as automatic timers, warning buzzers, etc. Therefore, one should consult the operation manuals supplied with the purchase of personal pumps. To learn how to operate, calibrate, repair, and maintain these devices. If desired, the pump which is purchased may be mounted to a tube tray to make the portable

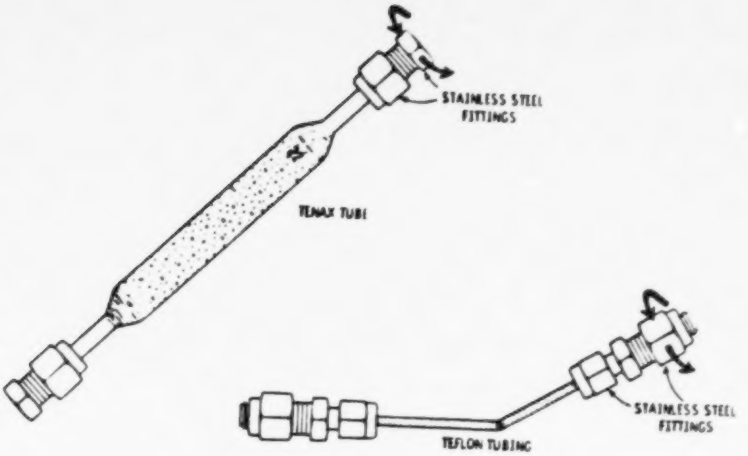

STAINLESS STEEL FITTINGS
22
TENAX TUBE
STAINLESS STEEL FITTINGS
TEFLON TUBING

Figure A-11. Remove cap from numbered end of a Tenax tube, and plug from one end of a stainless steel/ teflon connector.

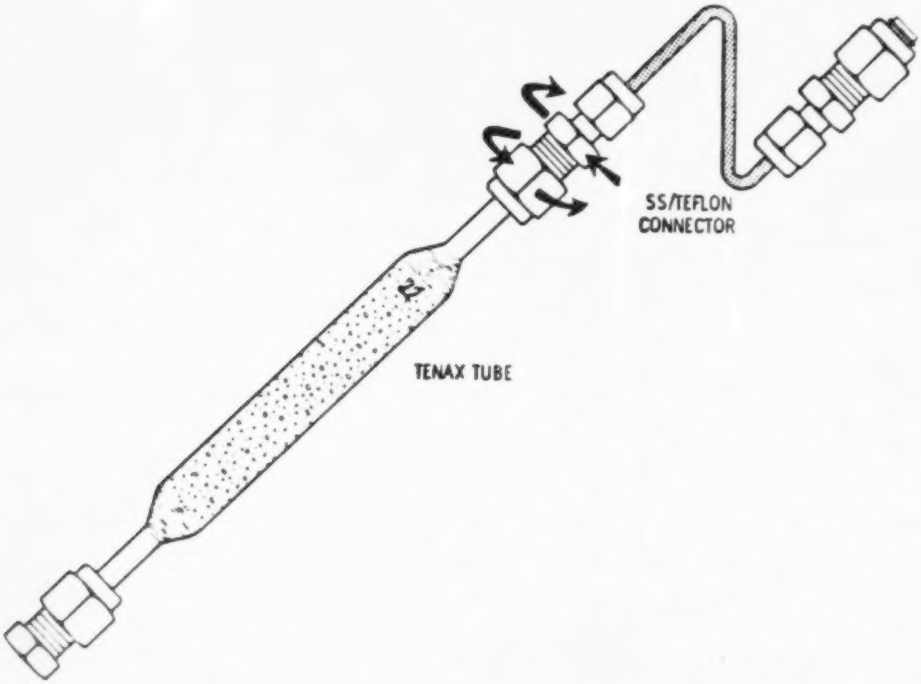

SS/TEFLON CONNECTOR
22
TENAX TUBE

Figure A-12. Attach the Tenax tube to the opened end of the stainless steel/teflon connector. Tighten with wrenches.

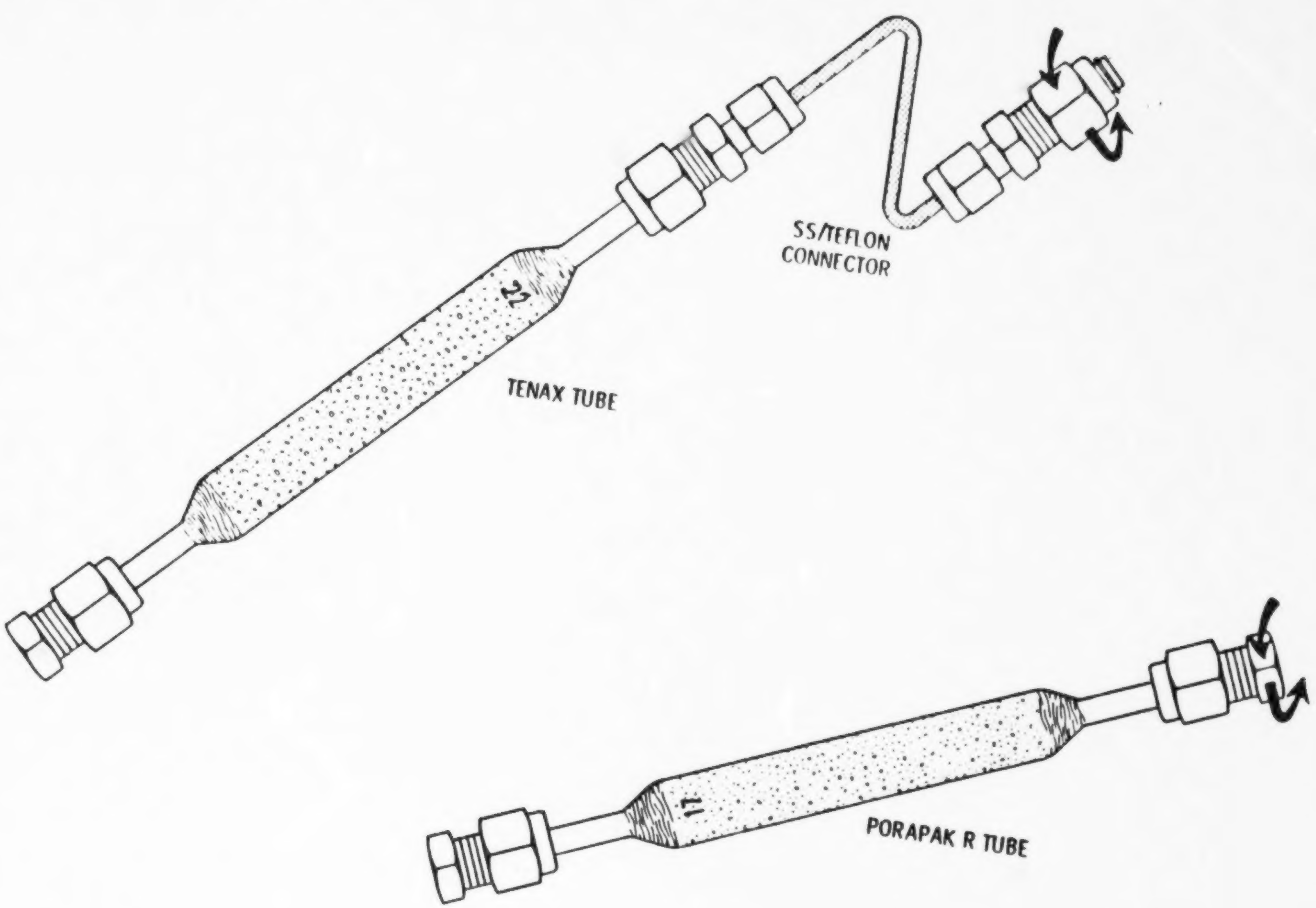

SS/TEFLON CONNECTOR
22
TENAX TUBE
17
PORAPAK R TUBE

Figure A-13. Remove plug from other end of stainless steel/teflon connector and the cap from the non-numbered end of a Porapak R tube.

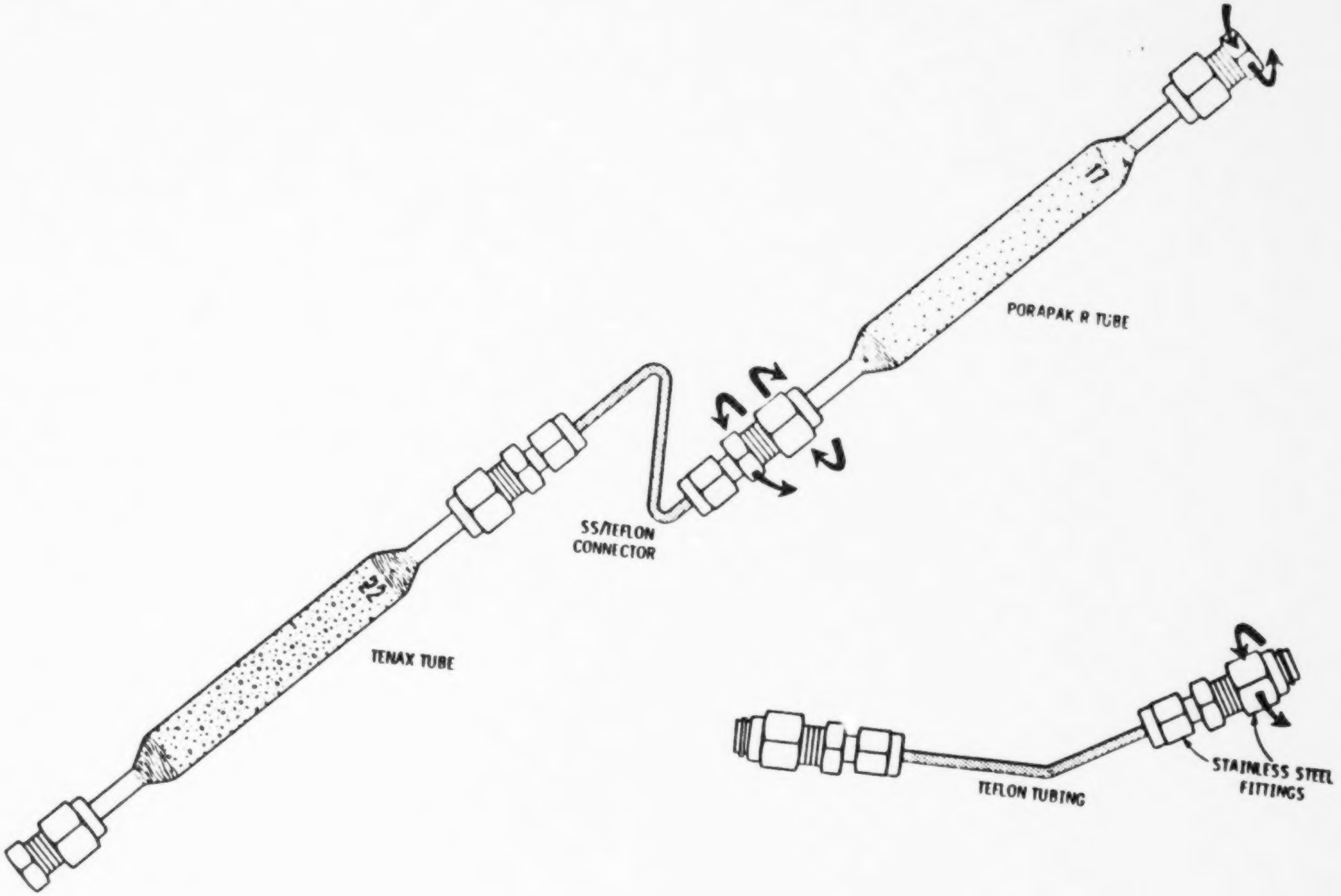

17
PORAPAK R TUBE
SS/TEFLON CONNECTOR
22
TENAX TUBE
TEFLON TUBING
STAINLESS STEEL FITTINGS

Figure A-14. Attach the Porapak R tube to the remaining end of the first stainless connector. Tighten with wrenches. Then remove cap from the other end of the Porapak R tube and a plug from one end of a second stainless steel/teflon connector.

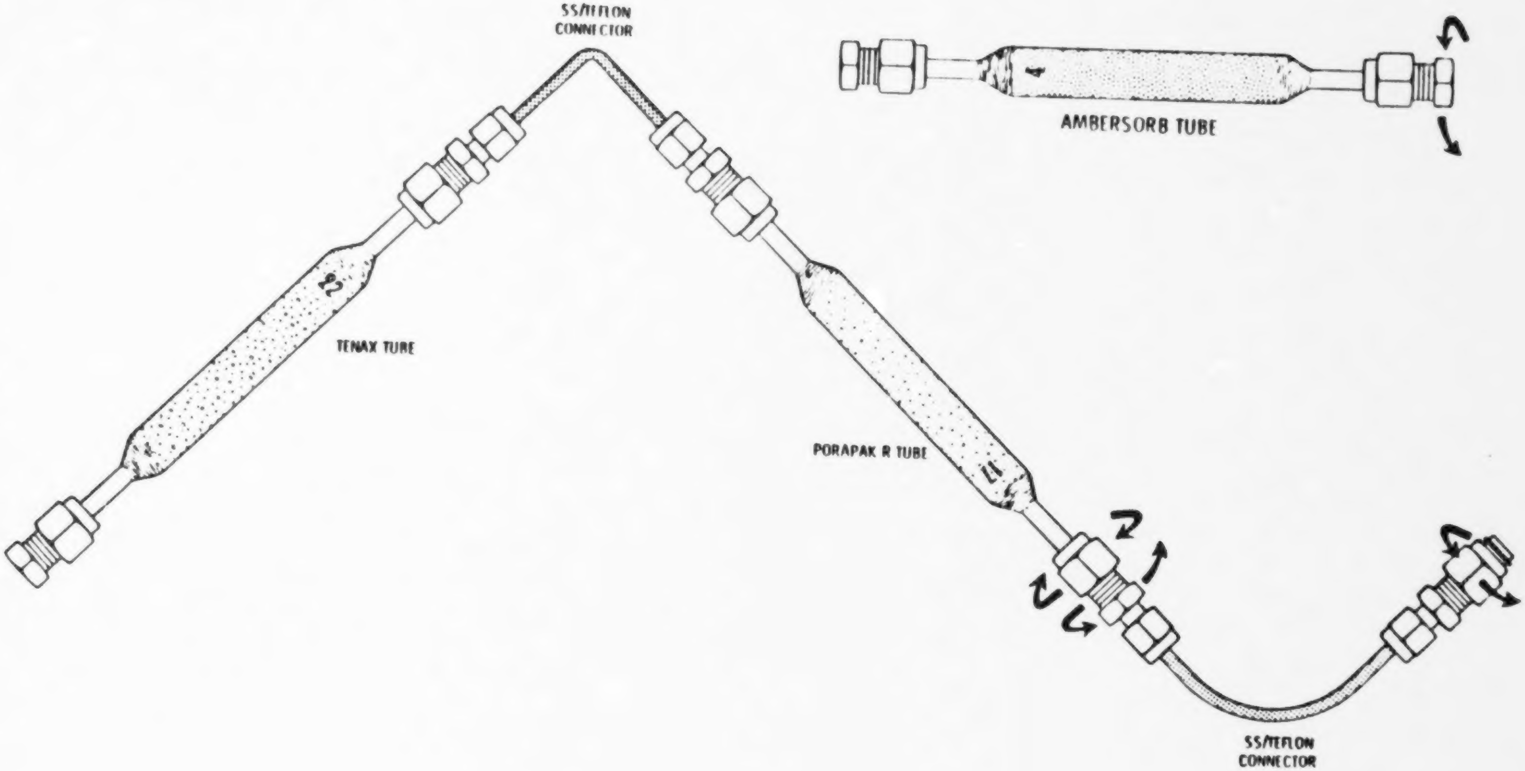

SS/TEFLON CONNECTOR
AMBERSORB TUBE
4
82
TENAX TUBE
PORAPAK R TUBE
17
SS/TEFLON CONNECTOR

Figure A-15. Attach the Porapak R tube to the opened end of the second stainless steel/teflon connector. Tighten with wrenches. Then remove the plug from the other end of the stainless steel/teflon connector and the cap from the non-numbered end of an Ambersorb tube.

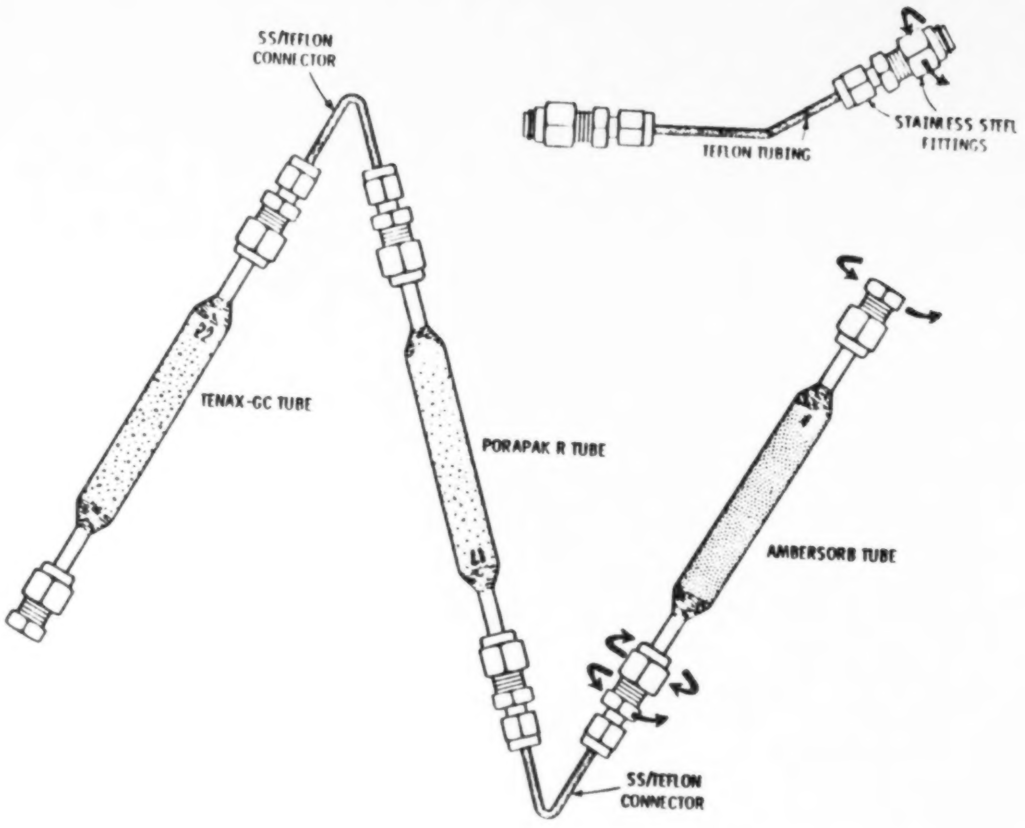
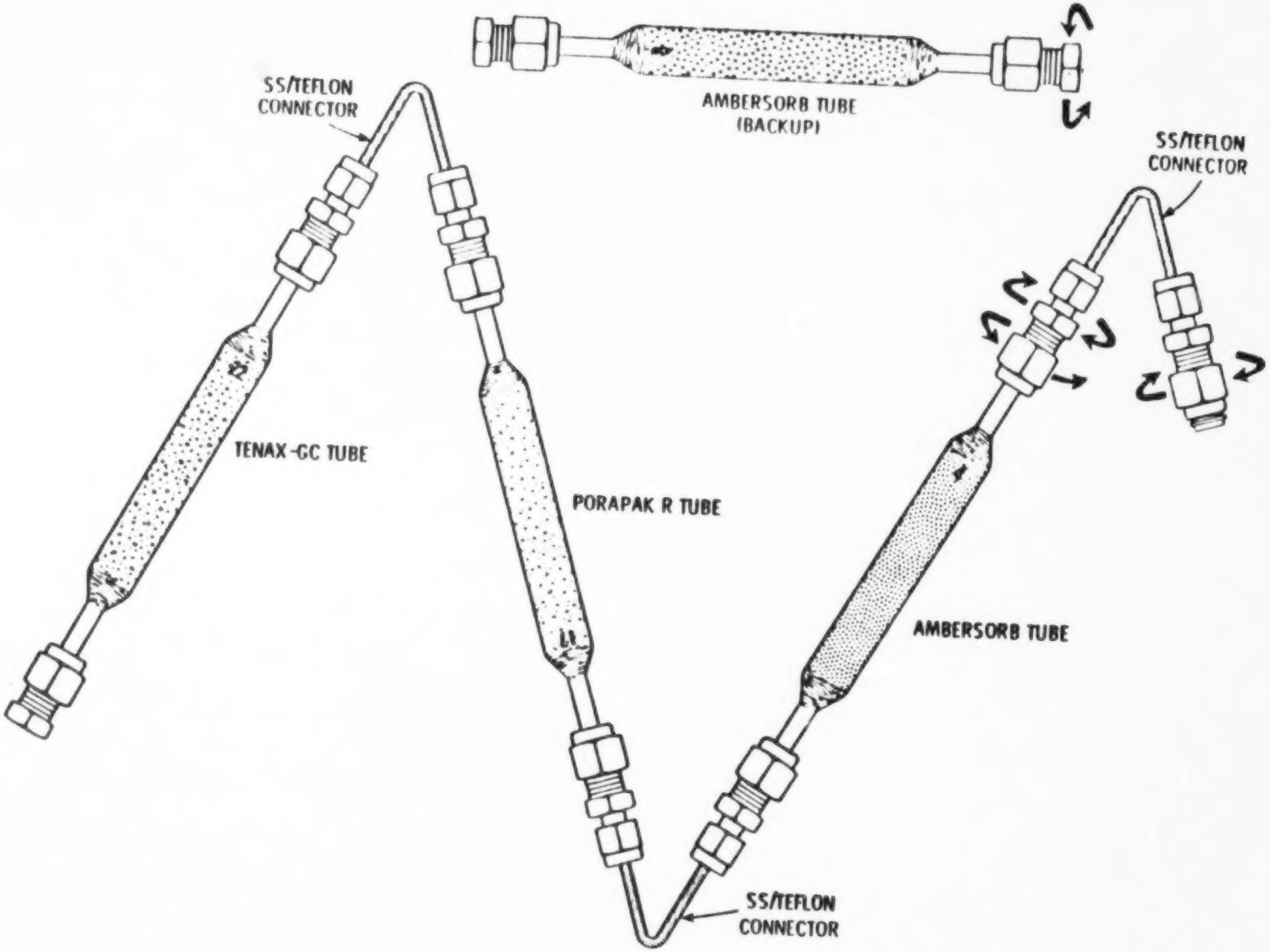

SS/TEFLON CONNECTOR
TEFLON TUBING
STAINLESS STEEL FITTINGS
TENAX-GC TUBE
PORAPAK R TUBE
AMBERSORB TUBE
SS/TEFLON CONNECTOR

Figure A-16. Attach the Ambersorb tube to the remaining end of the second stainless steel/teflon connector. Tighten with wrenches. Then remove the cap from the other end of the Ambersorb tube and a plug from one end of a third stainless steel/teflon connector.



AMBERSORB TUBE
(BACKUP)
SS/TEFLON
CONNECTOR
SS/TEFLON
CONNECTOR
TENAX-GC TUBE
PORAPAK R TUBE
AMBERSORB TUBE
SS/TEFLON
CONNECTOR

Figure A-17. Attach the Ambersorb tube to the opened end of the third stainless steel/teflon connector. Tighten with wrenches. Then remove the plug from the other end of the third stainless steel/teflon connector and the cap from the non-numbered end of a second Ambersorb tube (backup).

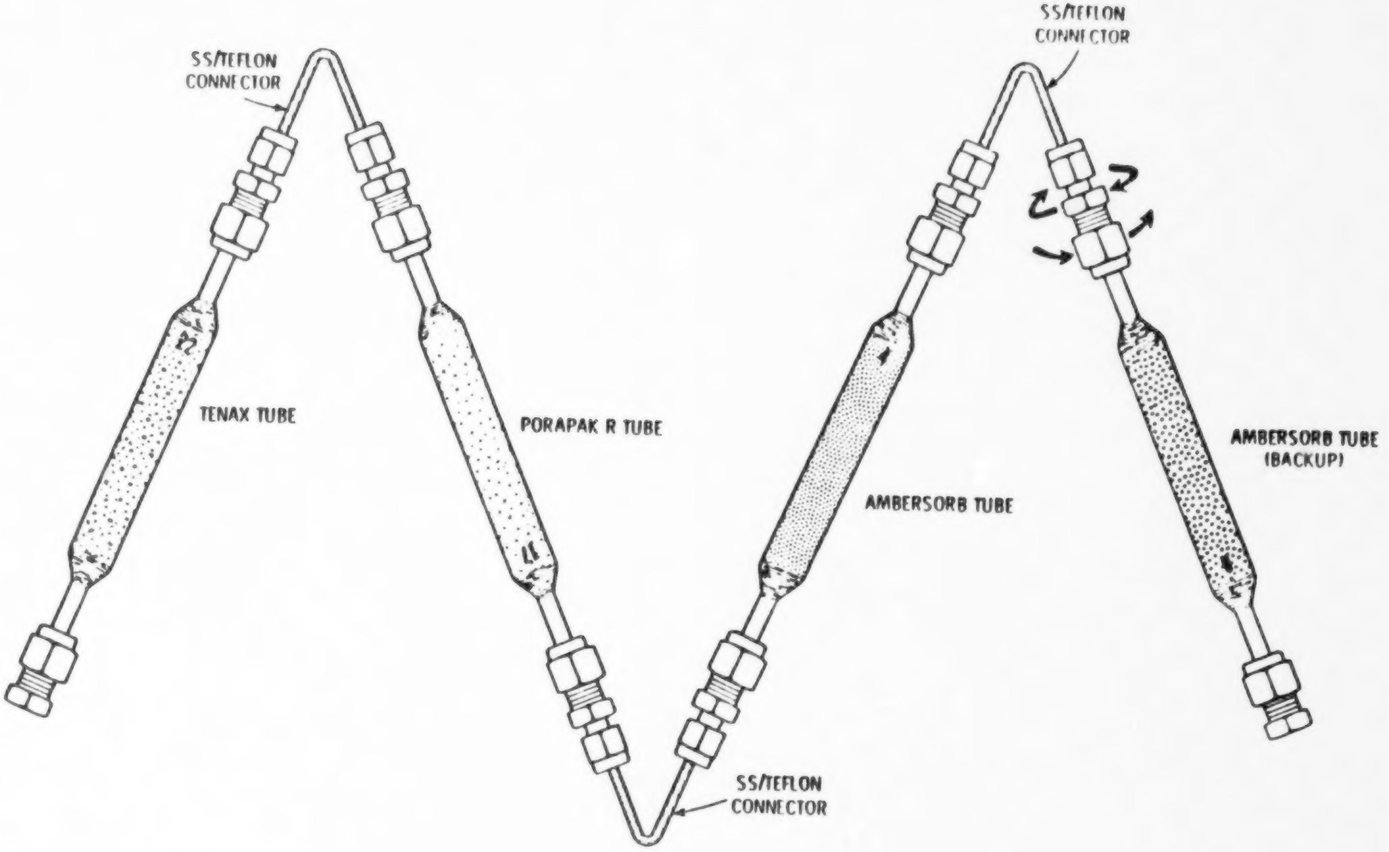

SS/TEFLON CONNECTOR
TENAX TUBE
PORAPAK R TUBE
SS/TEFLON CONNECTOR
AMBERSORB TUBE
SS/TEFLON CONNECTOR
AMBERSORB TUBE (BACKUP)

Figure A-18. Attach the backup Ambersorb tube to the remaining end of the third stainless steel/teflon connector. Tighten with wrenches.

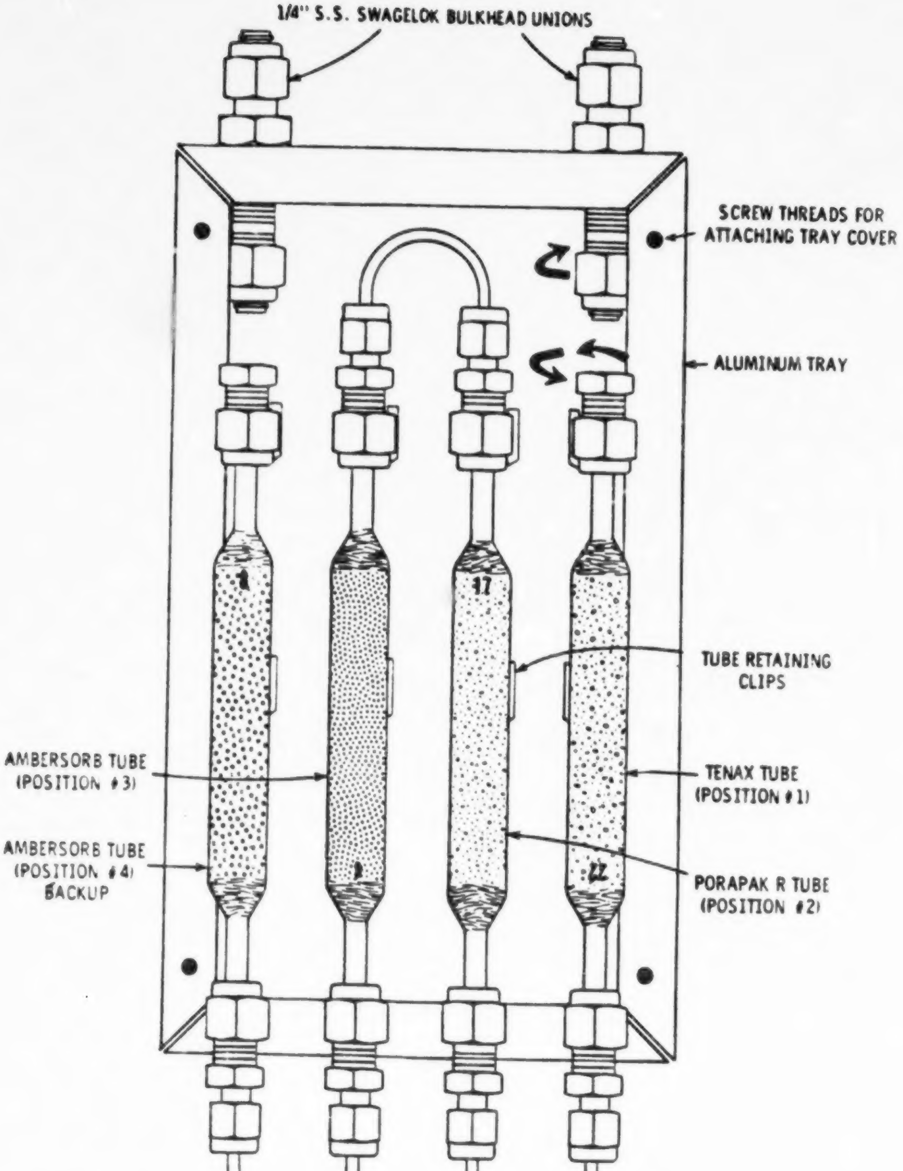

1/4" S.S. SWAGELOK BULKHEAD UNIONS
SCREW THREADS FOR ATTACHING TRAY COVER
ALUMINUM TRAY
TUBE RETAINING CLIPS
17
22
AMBERSORB TUBE (POSITION #3)
TENAX TUBE (POSITION #1)
AMBERSORB TUBE (POSITION #4) BACKUP
PORAPAK R TUBE (POSITION #2)
SS/TEFLON CONNECTORS

Figure A-19. Place series of sorbent tubes near the aluminum tube tray as shown above. Remove the plug from the inside portion of the right and bulkhead union and remove the cap from the free end of the Tenax tube.

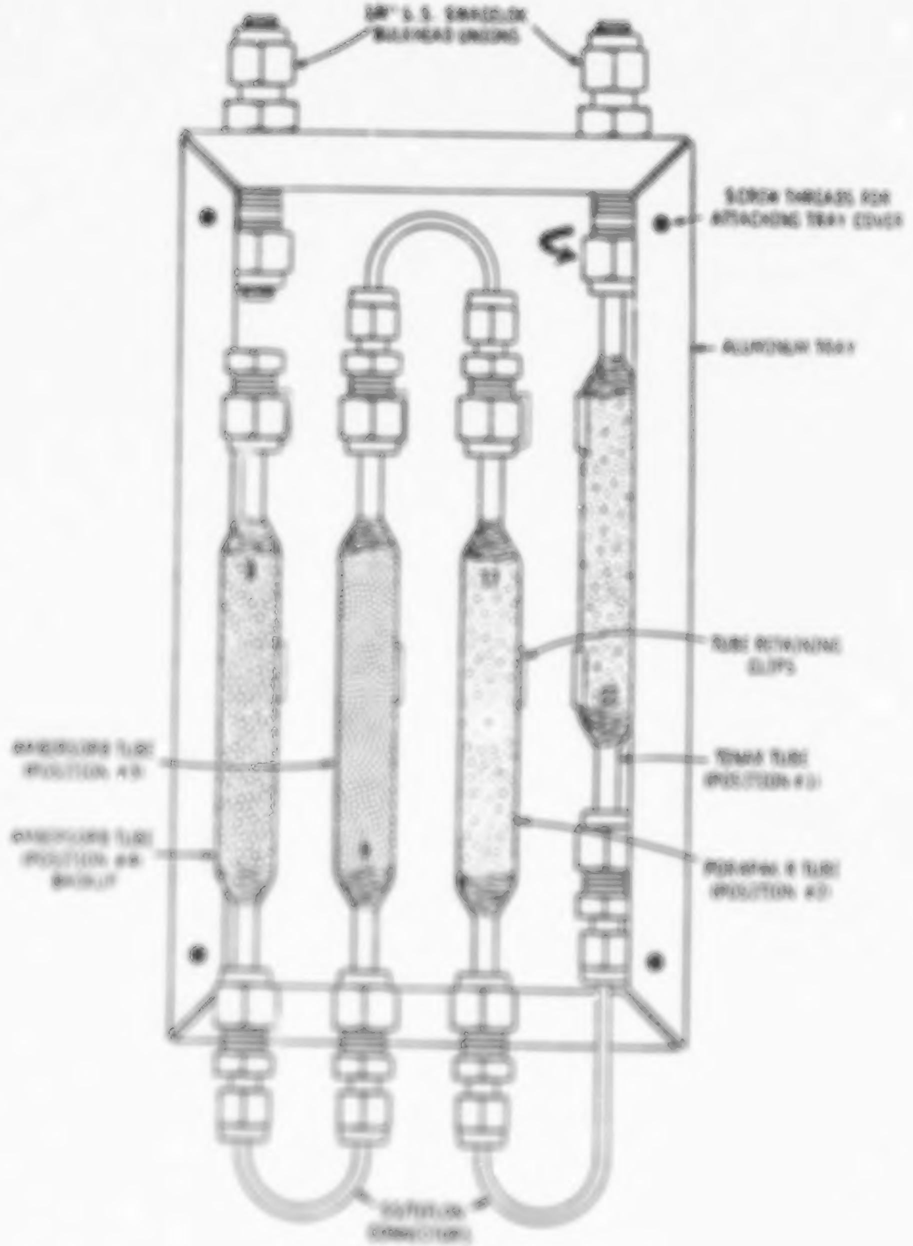
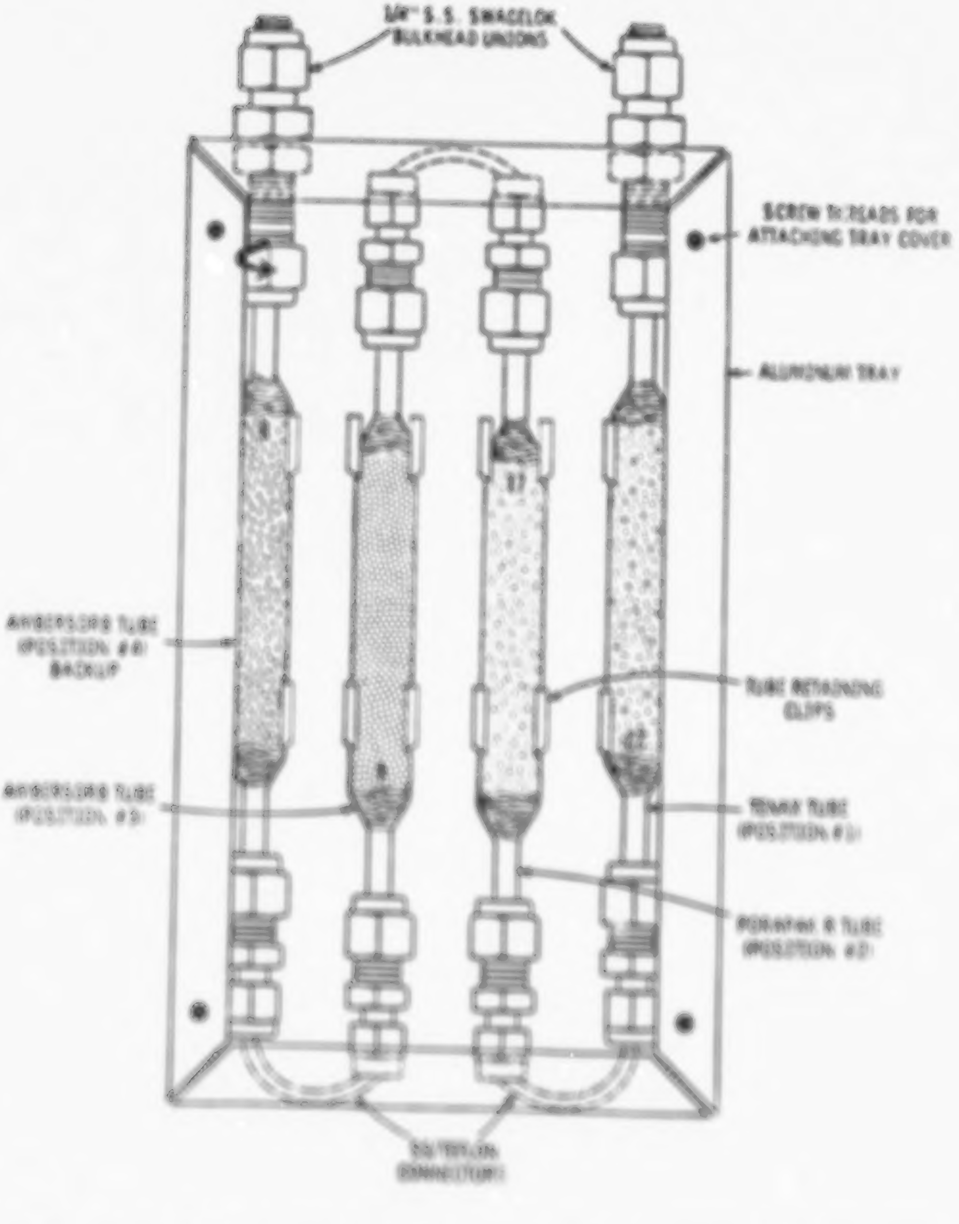

1/4" S.S. SWAGELOK BULKHEAD UNIONS
SCREW THREADS FOR ATTACHING TRAY COVER
ALUMINUM TRAY
TUBE RETAINING CLIPS
AMBERSORB TUBE (POSITION #3)
TENAX TUBE (POSITION #1)
AMBERSORB TUBE (POSITION #4 BACKUP)
PORAPAK R TUBE (POSITION #2)
TEFLON CONNECTIONS

Figure A-20. Carefully slip the Tenax tube into the tube retaining clips in position #1. Slide the tube up to and attach to the opened bulkhead union. Tighten with wrench.



1/4" S.S. SWAGELOK BULKHEAD UNIONS
SCREW THREADS FOR ATTACHING TRAY COVER
ALUMINUM TRAY
AMBERSORB TUBE (POSITION #4) BACKUP
TUBE RETAINING CLIPS
AMBERSORB TUBE (POSITION #3)
TENAX TUBE (POSITION #1)
PORAPAK R TUBE (POSITION #2)
SS/TEFLON CONNECTORS

Figure A-22. Carefully clip the second Ambersorb tube (backup) into the tube retaining clips in position #4. Slide the tube up to and attach to the opened bulkhead union. Tighten with wrenches.

miniature collection system into a single unit. There should be a belt clip or some other means of attaching the pump to an individual.

Prior to field sampling the pump should be checked for proper operation. As described later, the pump should be attached to a loaded "calibration" tube tray and leak checked. Then the "calibration" tube tray inlet should be opened, the pump flow controls set to their maximum, and the pump turned "on." Usually this will cause the pump to be under conditions beyond its specifications and capabilities. In other words the pressure drop across the "calibration" tube tray is too great for the pump to draw air across at its maximum flow setting. Therefore, the pump will show signs of stress, such as a "no-flow" indicator light "on," a buzzer sounding, irratic pumping behavior, etc. The pump should be turned "off," its flow slightly reduced, and then turned back "on." This procedure should be repeated until a flow rate setting is obtained at which the pump operates properly. This flow rate should be measured with a calibrated [50] bubble meter at the "calibration" tube tray inlet and pump exhaust. This flow rate represent the maximum attainable flow rate of the pump with the portable miniature collection system. This maximum flow rate may reduce with time and use of the pump. If the maximum flow rate is 30% or more below the original maximum flow rate, then the pump should undergo routine maintenance to improve pump performance.

Next the flow rate to be used during field sampling should be calculated. This flow rate should be 20% to 50% less than the maximum attainable flow rate to reduce stress on the pump and to allow for pressure drop changes across the sampling system (such as due to accumulation of water) during sample collection. The flow rate of the pump attached to the calibration tube tray should be set to the sampling flow rate and ran for at least an hour to assure proper operation of this flow rate.

In the field, prior to sample collection, the battery packs of the personal pumps should be fully charged. Extra charged packs are a nice convenience should battery power in the pumps begin to fail prior to completing sample collection. After the batteries are charged, the pump (only) should be set to the sampling flow rate, as measured by its exhaust. If possible, extra pumps should always be taken on a field sampling trip as replacements in case a pump should fail.

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[50] "Quality Assurance Handbook for Air Pollution Measurement Systems, Vol. II", U.S. Environmental Protection Agency, May 1977.

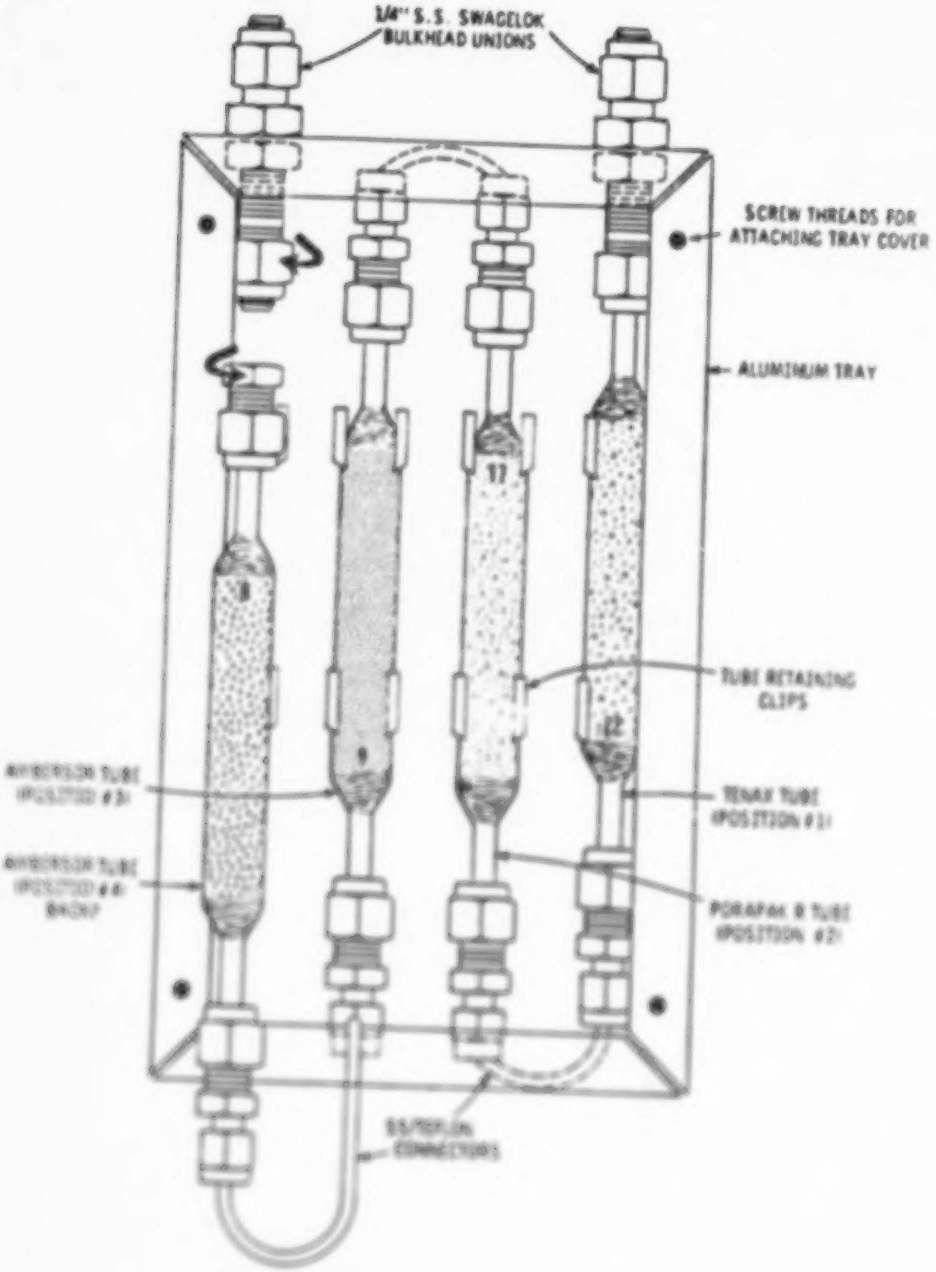
1/4" S.S. SWAGELOK BULKHEAD UNIONS
SCREW THREADS FOR ATTACHING TRAY COVER
ALUMINUM TRAY
TUBE RETAINING CLIPS
AMBERSORB TUBE (POSITION #3)
AMBERSORB TUBE (POSITION #4) BACKUP
TENAX TUBE (POSITION #1)
PORAPAK R TUBE (POSITION #2)
SS/TEFLON CONNECTORS
11
12

Figure A-21. Carefully slip the Porapak R tube and the first Ambersorb tube into the tube retaining clips in positions #2 and #3. Remove the plug from the inside portion of the left-hand bulkhead union and remove the cap from the free end of the second (backup) Ambersorb tube.

Calibration and Operation of the Portable Miniature Collection System

Before the portable miniature collection system is used for sample collections, several tasks should be performed. One task is to prepare a pump/tray connector such as depicted in Figure A-23. This hardware should be cleaned by the procedures described previously for cleaning hardware materials for sample tube storage. This connector may be placed in the tube tray of the portable miniature collection system, along with the stainless steel/teflon sorbent tube connectors, for transportation into the field. Also, a second, unattached tube tray should be "loaded" with four sorbent tubes (not necessarily freshly conditioned) in the manner described in the previous section. This tray will be used for measuring the flow rate of a small personal pump prior to sample collection. The "calibration" tube tray may be transported into the field while "loaded", since some contamination of the tubes is unimportant as they will not be analyzed. Finally, any solutions to be used for spiking the samples collected should be prepared in the laboratory prior to field sampling.

When going into the field to collect ambient air samples, at least the items listed below should be taken.

1) Portable Miniature Collection Systems with small personal pumps, tube trays, and all necessary connectors.

2) Power cord and/or battery chargers for the personal pumps and an extension cord.

3) A sufficient number of stored, freshly conditioned sorbent tubes (as determined by the sampling plan, which will be discussed later).

4) A bubble meter, stop watch, and calculator for flow rate calibrations.

5) A "calibration" sorbent tube tray.

6) A stopwatch or wrist watch for measuring the sampling times.

7) Necessary tools, including wrenches, screw drivers, and hex key.

8) Clean, silanized glass wool for particulate plugs for each sample.

9) Vials for containing the glass wool plugs after sample collection.

10) Spiking solutions and clean syringes.

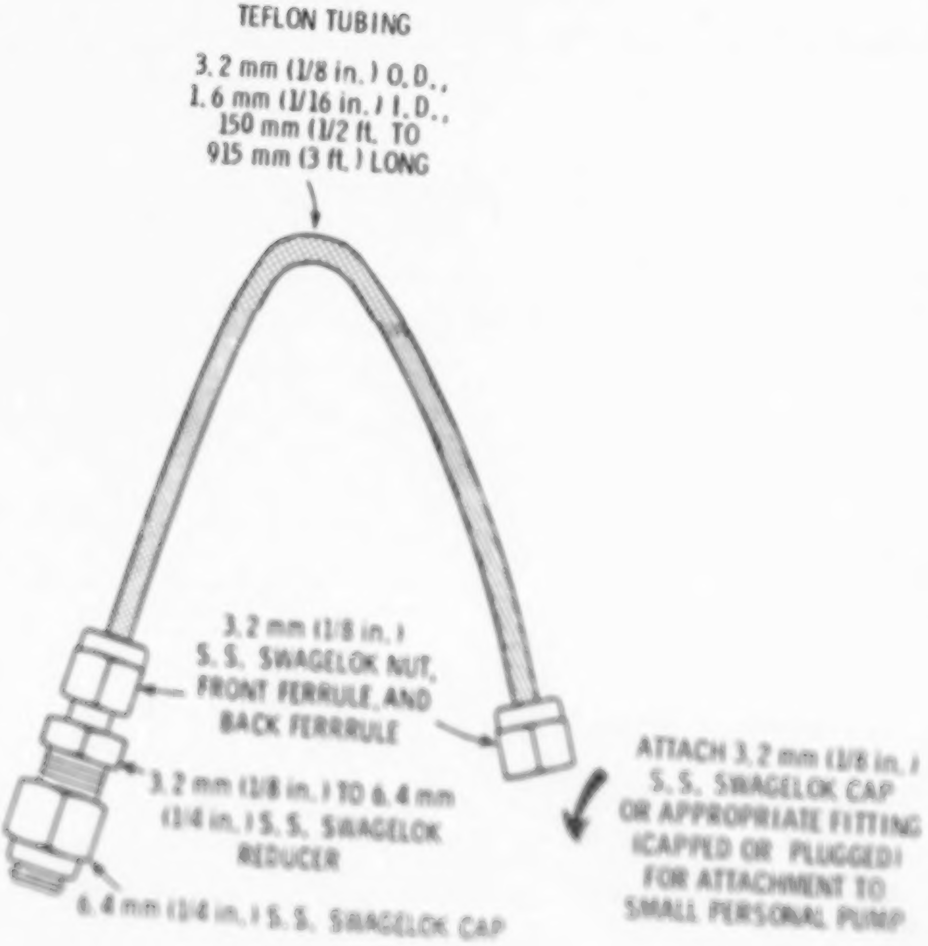
TEFLON TUBING
3.2 mm (1/8 in.) O.D.,
1.6 mm (1/16 in.) I.D.,
150 mm (1/2 ft. TO
915 mm (3 ft.) LONG
3.2 mm (1/8 in.)
S. S. SWAGELOK NUT,
FRONT FERRULE, AND
BACK FERRRULE
3.2 mm (1/8 in.) TO 6.4 mm
(1/4 in.) S. S. SWAGELOK
REDUCER
6.4 mm (1/4 in.) S. S. SWAGELOK CAP
ATTACH 3.2 mm (1/8 in.)
S. S. SWAGELOK CAP
OR APPROPRIATE FITTING
(CAPPED OR PLUGGED)
FOR ATTACHMENT TO
SMALL PERSONAL PUMP

Figure A-23. Pump/tray connector.

11) Thermometer and hydrometer (and any other meteorological equipment desired) for evaluating the sampling conditions.

12) "Sampling Fact Sheets" and a pen.

13) This manual!!

14) Necessary boxes, trunks, tape, and packing materials for transporting the above items.

15) Any required paperwork (e.g., shipping receipt, etc.).

Once in the field, before sample collection is initiated the Portable Miniature Collection System should have its sampling flow rate measured with a calibrated bubble meter. The bubble meter may be attached to the exhaust of a small personal pump, and the exhaust flow rate monitored whenever necessary. This exhaust flow rate can be compared to the inlet flow rate before and after sample collection. Measurement of the inlet flow rate must be taken with a "calibration" tube tray attached to the personal pump (see Figure A-24) in order to approximate the pressure drop incurred with a sorbent tube tray in this position during actual sampling and to prevent the contamination of the pump with surfactants. This tube tray should be quickly leak-checked as described below. With the flow of the pump at its previously set, desired flow rate, the pump should be turned "on." The flow at the inlet of the "calibration" tube tray should be measured with the bubble meter at least three times. This should be compared with exhaust flow rates, and all flow rate values recorded. This procedure is used, in conjunction with exhaust flow rate determinations, to determine the approximate sampling flow rate and to detect any major changes in this flow rate during sample collection. The flow rate should be adjusted to obtain the desired sampling flow rate through the tube tray inlet. If the pump is not operating properly at this flow rate (e.g., flow restriction indicator lit, low flow buzzer sounding, etc.), then reduce the flow rate until proper operation is obtained or a definite pump malfunction is determined. The flow rate can be used to determine a sample volume. Other conditions of the personal pump, such as valve or drive belt positions should be recorded during its "calibration" for comparison with the conditions used during sample collection.

With a tube tray attached to a small personal pump, a leak check must be performed to assure that air is being drawn only though the tray inlet. Since air is being drawn, not pushed, through the sorbent tubes and various connectors during sampling or calibration, a vacuum is created at any leak within the system. Therefoe, this system cannot be effectively leak-checked with a leak-detection liquid because that liquid would be drawn into the samplingsystem at the point of any leaks and contaminate that system. Howver,

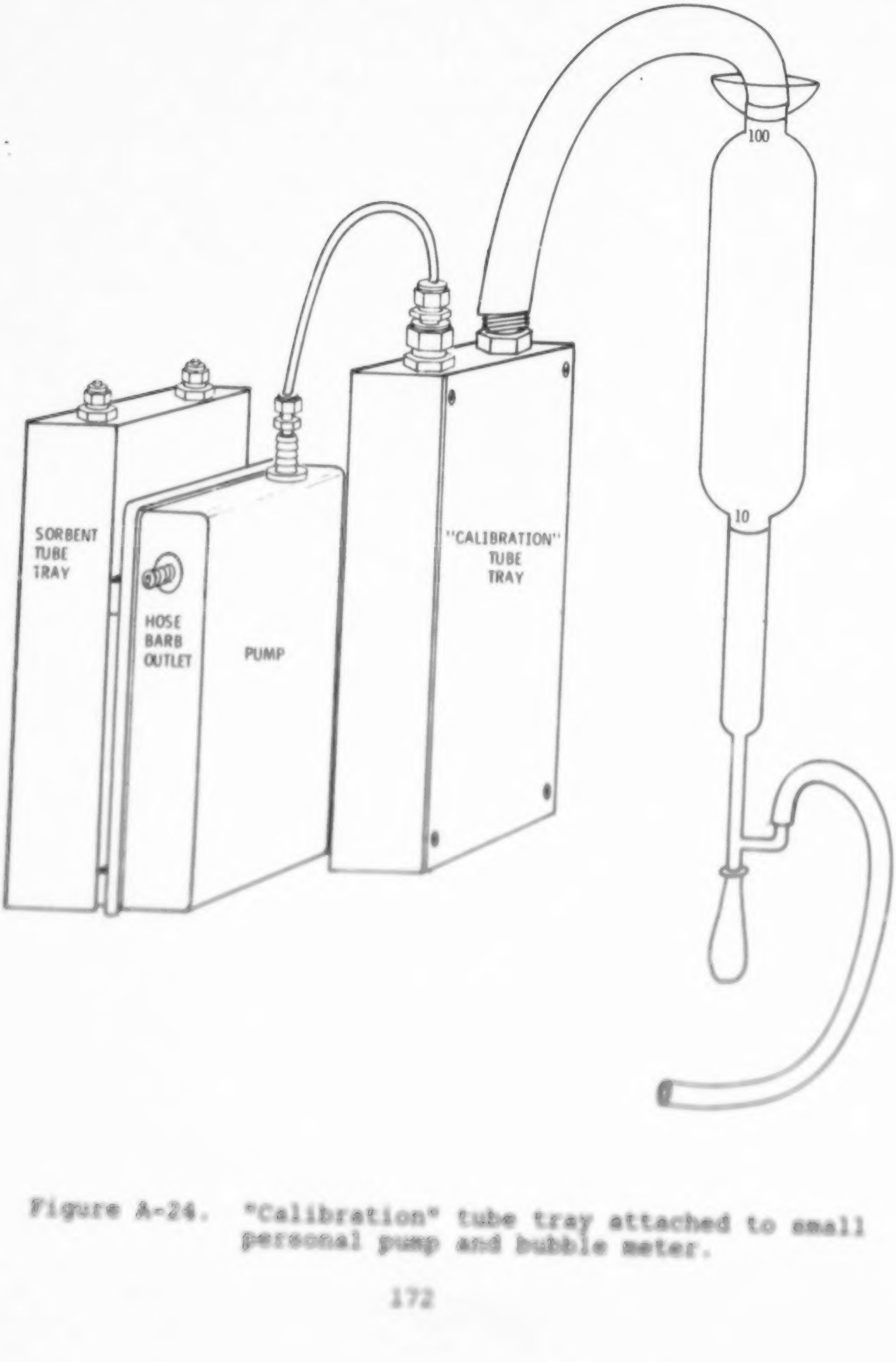
100
10
SORBENT TUBE TRAY
HOSE BARB OUTLET
PUMP
"CALIBRATION" TUBE TRAY

Figure A-24. "Calibration" tube tray attached to small personal pump and bubble meter.

the vacuum phenomenon can be successfully used to perform a "mechanical" leak check. This is done by first attaching the pump/tray connector to the personal pump with the end to be attached to the tube tray still capped. With a bubble meter attached to the exhaust of the pump, the system should be turned "on". The connector and pump should be quickly evacuated and no flow observed if no leaks are present within the system. If flow is observed, tighten all fittings until none is evident. Check internal connections within the personal pump, if necessary. The personal pump should be quickly turned "off" after a leak free system is obtained. The pump/tray connector is then attached to the tube tray ("calibration" or sample) outlet, with its inlet still capped (see Figure A-25). The above procedure is then repeated. If all connections were made securely when the tube tray was assembled, a relatively leak-free system should result. If a flow rate of less than 5 mL/min is observed, then the leak-check should be considered "acceptable". A flow of 5 mL/min through small leaks is insignificant compared to the sampling flow rate of 0.5 or 1 L/min. The results of the leak check should be recorded and the pump turned "off" prior to opening the tube tray inlet.

After calibrating the flow rate of the Portable Miniature Collection System, the final preparation should be made for sample collection. With the pump turned "off", the "calibration" tube tray should be removed from the pump/tray connector and replaced with a sorbent tube tray, "loaded" with four sorbent tubes according to the procedures described previously. Care should be taken to assure that all connections are secure by leak-checking the sampling system by the above procedure.

Now the Portable Miniature Collection System is ready for sample collection. First, the sampler should be placed in an appropriate location, such that the sorbent tube tray is not exposed to the exhaust of the personal pump. Next, the inlet plug of the tube tray should be removed and a small amount of glass wool inserted in this inlet to serve as a particulate filter. The portable ambient air sampler should be turned "on" by switching the appropriate switches. The time of sample initiation and all conditions of the personal pump should be recorded. Approximately every other hour after sampling is initiated, the conditions of the personal pump should again be checked and recorded. Exhaust flow rates should be determined at least every other hour. This will allow the approximate flow rate to be averaged over the sampling time to obtain a sample volume. The only other disturbance to the portable sampling system during sample collection, should be sample spiking, if required for the sample by the sampling plan. Both the techniques of sample spiking and the development of a sampling plan will be discussed later in this manual.

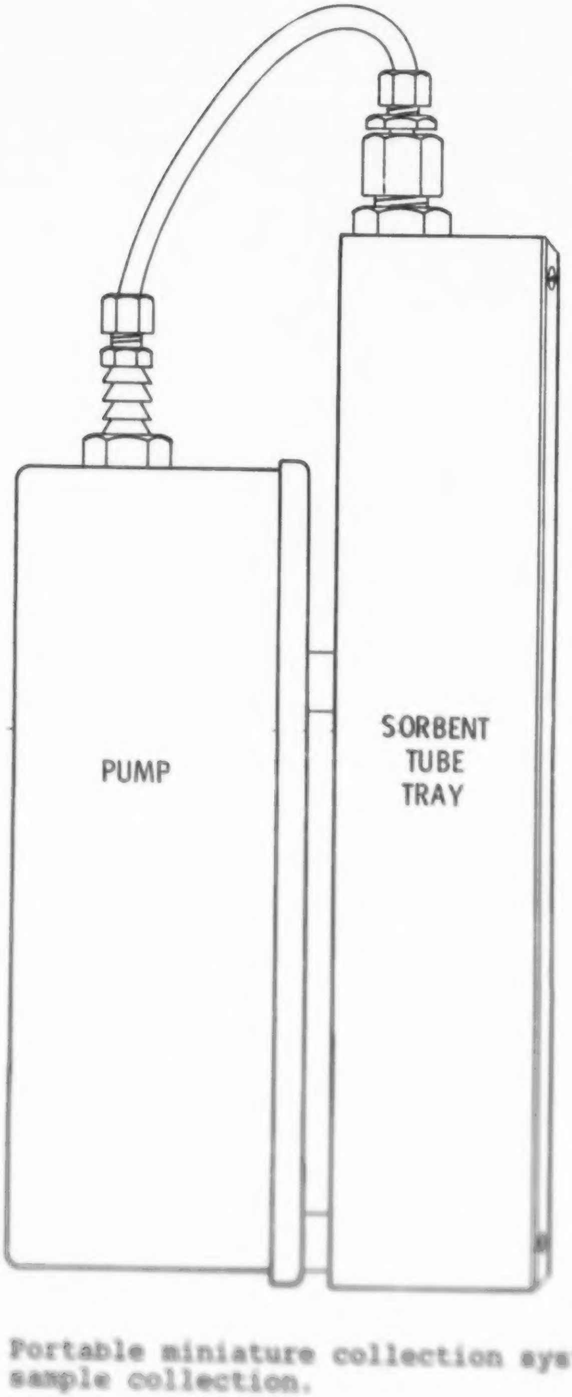
PUMP
SORBENT TUBE TRAY

Figure A-25. Portable miniature collection system ready for sample collection.

After sampling is complete (i.e., after 8 hrs.), the personal pump should be switched "off." Then the glass wool plug should be removed from the sorbent tube tray inlet and stored in a glass vial. The tray inlet should be plugged, the system quickly leak-checked, and the results recorded. The pump/tray connector should be removed from the sorbent tube tray, and the outlet of the tube tray plugged. The sorbent tube tray should be disassembled in the opposite manner of assembly with the sorbent tubes removed, capped, and placed in their appropriate culture tubes. Again, this should be done as quickly as possible to prevent additional sorbent contamination and to prevent loss of sample due to diffusion.

The flow rate through the personal pump should again be checked after sampling and after securing the sorbent tubes. This should be done by reconnecting the "calibration" tube tray to the personal pump, quickly leak-checking and determining the flow rate at the "calibration" tray inlet as previously described. This should be determined with at least three trials, and all flow rates (inlet, exhaust, and rotameter) and conditions recorded. This will allow a direct comparison to the conditions originally determined prior to sample collection.

Quality Control Considerations

In order to assure that data obtained from sorbent samples are reasonable and valid, various aspects of quality control/quality assurance (QC/QA) must be maintained. One aspect of QC/QA which should be addressed is the demonstration that the laboratory, which will be performing the sampling and analyses of sorbent samples, is competent and follows accepted good laboratory practices. (A more extensive discussion of quality control procedures and considerations is presented in a special MRC-EASC publication [51].) To meet the demands for QC/QA of samples for numerous environmental and industrial hygiene programs, such a laboratory should develop and continuously improve a good laboratory practice program.

Another aspect of QC/QA involves testing the sorbent sampling/ analytical method presented by various quality control measures. This should be done to practically demonstrate the validity of the method and of the samples. These control measures include evaluating standards, blanks, replicate, splits, backups, and spikes. Standard solutions of mixtures of compounds of interest (to this project) or other compounds for instrument evaluation/calibration should be analyzed to allow quantitation of compounds present in samples to generate calibration curves, to check detector linearity, and to assure that the analytical instrument and method are functioning properly. "Blanks" are sorbent tubes that are treated in a manner identical to that used for the sorbent tubes on which samples are collected except that no sample is drawn. Such "blanks" can indicate problems with contamination (e.g., from transport) and/or sorbent degradation. By collecting multiple samples on a number of tubes under identical conditions, replicate samples are collected which can provide data for determining the precision of the sampling/analytical method. When thermally desorbing the sorbent tubes for analysis, the tube effluent can be split and recollected for subsequent analyses using the same or different analytical method. Such split samples can be used to verify analytical precision or to validate analytical results by analyzing them under different conditions or using columns with different liquid phases. To evaluate the overall sampling/analytical method, backup sorbent tubes, and laboratory and field spikes are analyzed. A backup sorbent tube (Ambersorb XE-340) is placed in the fourth position during sampling to collect compounds "breaking through" the first three sorbent tubes. The compounds analyzed on this backup tube are, therefore, the compounds which were not quantitatively retained by the three sorbent system. A spike is a sorbent tube with a known quantity of the compound(s) of interest loaded on it. If the loading is done in a laboratory after sample collection or on a "blank" sorbent tube, that tube is called a "laboratory" spike. If the loading is done before or during sample collection, that tube is termed a "field" spike. Laboratory spikes can indicate sample stability and lifetime to some extent, but they are mainly used to determine desorption-efficiencies. Whether or not the compound of interests is altered during sampling or lost for another reason should be indicated by the recoveries obtained for field spikes.

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[51] W. M Haynes, D. M. Haile, D. H. Toy, and W. M. Mees, "Guide to God Laboratory Practices", the Environmental Analytical Scieces Center, MRC, Dayton, Ohio, March 1979.

There are numerous procedures by which laboratory and field spikes can be produced. One technique is to simply "inject" a small quantity of an analytical standard solution into the "inlet" end of a sorbent tube or the inlet of a tube tray. Although this technique is very simple and cost-effective, problems can arise due to the solvent interfering with the analyses or changing the sorbent retention characteristics. Another technique is to generate a vaporous standard mixture and "load" a small amount of this mixture into the "inlet" end of a sorbent tube. Usually this spiking technique requires special equipment (see Appendix B) that is more easily operated in a laboratory. Under these conditions all spikes must be performed prior to field sampling. Whatever technique is used should be quickly evaluated in the laboratory prior to preparing a field sampling trip.

For this project each air sample is collected in a sorbent tube tray containing three or four sorbent tubes. The analysis times for these sorbent tubes ranges from 1 to 3 hours depending upon the sorbent type, the amount of material adsorbed, and the analytical technique. Therefore, there is a great deal of time and cost involved in the analysis of each air sample. An extensive quality control program, using a large number of sample replicates, spikes, splits, etc., would be extremely costly and, therefore, impractical. However, at least some quality control samples need to be collected and analyzed in order to demonstrate the validity of sample data, even if not enough are collected to specify the accuracy and precision of the sampling/analytical method. The best approach is to devise a sampling plan specifically designed for a particular sampling program, such that there are at least one set of blanks, a few splits, spikes, backups, replicates, and calibration/ quantitation standards.

The sampling plan which is devised for a field sampling program should describe the following information for each sorbent tube:

- Tube number and sorbent type.
- Purpose of the sorbent tube (blank, sample, replicate sample, lab transport spike, sample spike, field transport spikes, backup, etc.).
- The position of the tubes in a tube tray (if any).
- The sampling conditions (if any), including date, time, sample volume and flow rate.
- The pump and pump conditions, if sampling is done.
- Any additional, pertinent information, such as the identity and amount of spikes, as well as method and time of spiking, or additional tube purpose.

An example of such a sampling plan is given in Table A-4. The information given in this table should also be marked on the outside of each of the sorbents' culture tubes to prevent switching of sorbent tubes. Grouping tubes together according to purpose during packaging will also help to keep the sorbent tubes from getting mixed-up.

Storage, Transportation, and Contamination

This part of this manual briefly reviews and summarizes information on sorbent tube storage, transportation, and protection from extraneous contamination given previously in a number of different sections. Generally, there are five phases in using sorbent tubes to collect ambient air samples. The first phase is the preparation of the sorbent tubes for sample collection, including preparation of some sorbent tubes as quality control samples; second is the protective storage and packaging of the sorbent tubes, grouped according to the sampling scheme, for safe and rapid transport to the field sampling location; third is the collection of air samples at the field location, including preparation of additional quality control samples; fourth is the protective storage and packaging of the sorbent tubes for safe and rapid transport back to the laboratory for analysis; and fifth is the analysis of the field and quality control samples. At each stage of preparation, storage, and transport, the sorbent tubes need to be protected from contamination and other adverse phenomena (e.g., breakage, sunlight, excessive heat, etc.) which could affect the materials adsorbed on the tubes and, hence, the validity of their data.

In review, to prevent the contamination of the sorbent tubes with extraneous materials during their preparation, the following guidelines should be observed.

1) All glassware and other hardware materials used during sorbent tube preparation should be meticulously cleaned prior to preparing the sorbent tubes.

2) Hardware and other materials which will be used to prepare the sorbent tubes should never be handled with bare hands. Protective gloves and/or clean utensils should be used to handle these materials.

3) Ultra-high purity solvents should be used during the soxhlet extraction of sorbent materials and teflon tape on sleeves (not silicone grease) should be used to seal the glass joints of the extraction glassware.

4) A charcoal trap should be used in the vacuum line of a vacuum oven during the vacuum drying of the sorbent materials.

5) The environment to which the sorbent materials, or tubes are exposed should be as clean and dry as possible.

6) During the thermal conditioning of the sorbent tubes, the gas stream should be pre-purified by passing it through a drying trap and a charcoal trap.

7) After thermal conditioning, the sorbent tubes should be quickly capped and stored.

8) If a sorbent tube is to be spiked, the spiking solution or vaporous mixture should be carefully and "freshly" prepared, the spiking materials meticulously cleaned, and the spiking performed as quickly as possible.

After preparation, the sorbent tubes should be stored tightly capped with metal fixings and viton o-rings, and contained within culture tubes. They should be used to collect air samples within one week

TABLE A-4. FIELD SAMPLING PLAN

Tube #	Sorbent type	Purpose	Tray position	Sampling Date	Sampling Times	Sampling Volume	Sampling Flow rate	Other information
140	Tenax	Sample #1	1					
150	Porapak R	Sample #1	2	4/14	~8AM-~4PM	~480 L	~1 L/min.	Spectrex - pump #1
163	Ambersorb	Sample #1	3					
260	Ambersorb	Backup-Sample #1	4					
243	Tenax	Blank	-	-	-	-	-	
246	Porapak R	Blank	-	-	-	-	-	
156	Ambersorb	Blank	-	-	-	-	-	
238	Tenax	Calibration	1					
155	Porapak R	Calibration	2	4/14 & 4/15	-	-		
361	Ambersorb	Calibration	3					
158	Ambersorb	Calibration	4					
236	Tenax	Transport spike	-	-	-	-	-	Lab spike, method A spike #2, spiked @ 11:30 AM, 4/11/80
252	Porapak R	Transport spike	-	-	-	-	-	
265	Ambersorb	Transport spike	-	-	-	-	-	
141	Tenax	Sample #4 - spike	1					
249	Porapak R	Sample #4 - spike	2	4/15	~8AM-~4PM	~240 L	~0.5 L/min	Field spike, method B spike #2, spike 15 min after starting sampling DuPont pump #1
362	Ambersorb	Sample #4 - spike	3					
257	Ambersorb	Backup-sample #4 spike	4					
139	Tenax	Transport spike	-	-	-	-	-	Field spike, method A spike #2, spike ~3:00 PM 4/14/80
147	Porapak R	Transport spike	-	-	-	-	-	
359	Ambersorb	Transport spike	-	-	-	-	-	
337	Tenax	Xtra - "Blank"	-	-	-	-	-	To replace any other tubes broken (except lab transport spikes)
145	Tenax	Xtra - "Blank"	-	-	-	-	-	
351	Porapak R	Xtra - "Blank"	-	-	-	-	-	
248	Porapak R	Xtra - "Blank"	-	-	-	-	-	
264	Ambersorb	Xtra - "Blank"	-	-	-	-	-	
166	Ambersorb	Xtra - "Blank"	-	-	-	-	-	

after thermal conditioning. This insures sorbent background is at a minimal level during sample collection. In addition, all the sorbent tubes, stored the same way as described above, should then be analyzed at least within one month, preferably within two weeks, after sample collection. While being stored or transported the capped and contained sorbent tubes should be kept in an environment as clean and dry as is practical. Furthermore, they should not be exposed to excessively hot temperatures, which would induce sorbent degradation and/or in-situ sample reactions, or to excessively cold temperatures, which could cause a change in sorbent properties and/or condense water out of the collected samples. A cool environment, at approximately ambient temperatures (15°C to 25°C), would be preferable. The sorbent tubes should also be protected from light, especially sunlight, during storage and transport to prevent light-induced reactions or degradations. To help protect the sorbent tubes from breakage during transport, clean glass wool can be wrapped around the sorbent tubes within the culture tubes. These culture tubes can be labeled and grouped according to the field sampling plan, and packaged with protective packing materials (e.g., styrofoam, bubble-sheets, etc.) inside a box or small suitcase. Finally, all paperwork associated with the transport of the sorbent tubes, sampling systems, and associated supplied should be prepared in advance of a field sampling trip.

During sample collection, certain guidelines, which are similar to the ones described for sorbent tube preparation, should be followed to prevent the contamination of the sorbent tubes with extraneous materials. These guidlines are listed below.

1) All hardware materials used during sample collection should be meticulously cleaned prior to field sampling.

2) Protective gloves and/or clean utensils should be used when handling the sorbent tubes during field sampling. Furthermore, extra care should be taken not to touch or otherwise contaminate the sorbent tube ends.

3) The sorbent tube tray should be assembled quickly, with the sorbent tubes exposed to the atmosphere as little as possible.

4) All fittings should be securely tightened with wrenches. They should be leak-checked according to the procedure previously described, not with a leak-detection fluid since this can contaminate the sorbent tubes.

5) If a sorbent tube is to be spiked, with a spiking solution, the solution should be carefully and "freshly" prepared, the spiking materials meticulously cleaned, and the spiking performed as quickly as possible.

6) The tube tray lid should be on the tube tray during sampling to protect the sorbent tubes from sunlight.

7) If possible, the sorbent tube tray should be kept out of "hot" locations during sampling. For example, sampling should be done in a shaded location rather than on asphalt or concrete in hot, direct sunlight.

8) Sampling should be performed in a location away from sources of atmospheric contamination (e.g., cigarette smoke, fumes from automobile and truck exhausts, flowers, etc.), if they are not of interest.

Records

As mentioned numerous times in this manual, it is necessary to keep accurate, detailed records of all aspects of sorbent sampling. These records should include information on the history of each sorbent tube, the sampling schemes for each sampling program, all sampling conditions and flow rates, the sorbent tube storage and transportation conditions, the log in and transfer of samples, and the analytical methods, conditions, and results. All of these records help to insure the accuracy of the final results obtained and/or to identify the cause of any problems or discrepancies observed during sampling or in the analytical results.

The purpose of keeping histories for each sorbent tube is to allow the quick review of how and when the tube was prepared, and how, when, and what types of samples to which the sorbent tube was exposed after preparation. This allows variations in sampling results to be traced to variations in the histories of the sorbent tubes used in a particular sampling program. Furthermore, accurate histories help to prevent sorbent tubes from getting "mixed-up", from being stored for unreasonably long periods of time (e.g., 5 years), or from being used an unreasonable number of times (e.g., 1000 times) for collecting samples. The information that should be recorded in a sorbent log-book while preparing sorbent tubes was given previously Figure A-7, in this manual. Such records should be kept for each sorbent tube. In addition, information such as shown in Figure A-26 should also be recorded in the sorbent log book for each sorbent tube each time it is used to collect a sample. Although not all the information shown may be available for all tubes and all samples, the sorbent log book should be kept as complete as possible.

For field sampling, record-keeping begins with the development of a sampling plan, as discussed previously. This sampling plan is used as a master scheme to coordinate sampling and sampling information. Information on all sampling conditions, including weather, flow rate, and sorbent cartridges, should be recorded on a sampling fact sheet for each sample specified in the sampling

"Sampling Lifetime"

Name:

Tube #: Sorbent Type: Date Packed:
Last Conditioning Procedure:
Date:
Storage Procedure:
Storage Dates:
Transportation Procedure:
Packaging Procedure:
Lab to Field Dates: Field to Lab Dates:

Sampling Conditions

Sampling Date: Sampling Fact Sheet #:
Type of Sample: Lab Blank Field Blank Lab Spike
Backup Transport Spike Field Sample Spike
Field Sample
Log In Date: Log In #:
Analysis Request #: Analysis Request Date:
Analysis Procedure:

Analysis Dates Name:
Analytical Results (briefly):

Analytical Results Reference (NB. Pg. or Report #):

Date Sample Log Closed:

Sorbent Cartridge Fate

Storage Procedure: Dates:
Reconditioning Procedure:
Reconditioning Date:
Log Book Reference Pg:

Date Sorbent Tube Unpacked: Comment:

Recycled? Sorbent: Glass Cartridge:
Log Book Pg:

Figure A-26. Information which should be recorded in a sorbent logbook.

plan. An example of such a sampling fact sheet which should be completed when collecting a sample with the portable miniature collection system is depicted in Figure A-27. A fact sheet should also be completed for each set of quality control samples. Keeping such detailed information during a field sampling program can help to define problems with the sampling technique and/or method. Information is also recorded in the fact sheets regarding sorbent tube storage, transportation, and transfer for analysis.

Once field sampling is completed and the sorbent tubes are received at a laboratory for analysis, these samples should be logged in through the laboratory's sample log-in system for proper transfer to analytical personnel. As part of that laboratory's quality control/quality assurance program, this sample log-in system should allow the easy review of the chain-of-custody (record of individual(s) charged with responsibility for these samples) of a set of samples and ready coordination of sorbent tube preparation, field sampling, and analytical information and reports.

Reconditioning Sorbent Cartridges

After collecting and analyzing a set of ambient air samples, the sorbent tubes can be reconditioned for subsequent sampling programs. This reconditioning can be done in one of two ways. The first method is simply to thermally condition the sorbent tubes as described in previously for the original preparation of these cartridges for sampling. This should be done soon after the sorbent air samples are analyzed in order to remove, as quickly as possible, any compounds from the sorbent tubes not removed during these analyses. This helps to insure that any compounds of the air sample still remaining on the sorbent tubes will not irreversibly adsorb on or cause the degradation of the sorbent materials. However, after the sorbent tubes are thermally reconditioned, a set of blanks should be analyzed to determine if the background of the sorbent tubes is "acceptable". To be "acceptable", these backgrounds should be the same types and levels as determined for the first air sample quality control blanks. If the reconditioned sorbent tubes are found to be "acceptable", they should be used for collecting another set of air samples within one week of being thermally conditioned, or be thermally conditioned again immediately prior to the next sampling program.

If the sorbent tube backgrounds are found to be unacceptable, or if these tubes have been used to collect a number of air samples (~5), then a second, more rigorous, reconditioning method should be used to rejuvenate the sorbent materials. By this method, after the sorbent tube air samples have been analyzed, the sorbent tubes should be "unpacked". The glass wool plugs retaining the sorbent materials within the sorbent tubes should be removed and discarded. The sorbent materials should be "poured" into clean glass jars, keeping the different sorbent materials separate.

PORTABLE MINIATURE COLLECTION SYSTEM:

SAMPLING FACT SHEET #___

Date of Sampling: Name(s):

Location (City, State, Street, Etc.):

Atmospheric Conditions:

TYPE OF SAMPLE Lab Blank Field Blank Lab Spike
Transport Spike Field Sample Spike Field Sample Sample Backup
Spike Backup Calibration

SORBENT CARTRIDGES

Tube #	Sorbent Type	Condition of Cartridge	Tray Position	Comments

IF SPIKE: Date Spiked: Notebook Page:

Procedure:

Amounts & Names of Compounds:

PUMP CONDITIONS Power: AC DC No. of Valve Turns:

Other:

Initial Time: Final Time:

Figure A-27. Sampling fact sheet.

Flow Rate Observed for System Calibration and Sample Monitoring

		Time for mL of flow, min			Average Flow Rate, mL/min	Temperature, °C
Setup	Time	Trial 1	Trial 2	Trial 3		

Figure A-27 (continued)

EVALUATION OF FLOW MEASUREMENTS

Location of Flow Measurement	Flow Rates mL/min			Sampling Time, min	Estimated Sample Volume, liters		
	Hi	Ave.	Lo		Hi	Ave.	Lo

TRANSPORTATION AND STORAGE

Storage Procedures/Conditions:

Transportation Procedures/Conditions:

Packaging Procedures/Conditions:

Lab to Field Dates:

Field to Lab Dates:

SAMPLE TRANSFER

Log-In Date:

Log-In #(s):

Analysis Request #:

Analysis Request Date:

Requestor:

Sent to:

Figure A-27 (continued)

The sorbent materials should be sieved (60 mesh for Tenax and Ambersorb, 80 mesh for Porapak R) to remove fine particles. Then the sorbents should undergo the extraction/drying procedures given previously for cleaning "new" sorbent materials. After cleaning and re-deactivating the glass cartridges (now empty) by the method given previously (discarding and replacing cartridges with badly broken ends), the sorbent materials are then "repacked" in the glass cartridges. These "re-packed" sorbent tubes should receive a new page in the sorbent log-book, with reference back to the original sorbent tubes, and should be indicated as "second generation" sorbent tubes. Within one week of the next sampling program these sorbent tubes should be thermally conditioned. The hardware materials for the storage of these sorbent tubes should also be re-cleaned according to the procedures given previously. (Hardware used within the sorbent tube tray or for connecting the pump and tube tray should be re-cleaned between each sampling program.)

Since each sorbent tube has a definite "lifetime" after which its capacity for retaining compounds diminishes or its background level becomes excessively high, limits must be placed on the number of times a sorbent can be used. For this project, a sorbent tube (with "acceptable" background) may be used to collect up to five air samples or be thermally conditioned up to fifteen times (whichever comes first), before being re-extracted or discarded. The sorbent materials may be re-extracted twice (i.e., three sorbent tube "generations") for rejuvenating these materials. This allows a total up to fifteen air samples, forty-five thermal conditionings, and three extractions for a lot of sorbent material.

Flow Chart II

The flow chart given in Figure A-28 summarizes the procedure for preparing the Portable Miniature Collection System, for collecting air samples, and for reconditioning sorbent tubes.

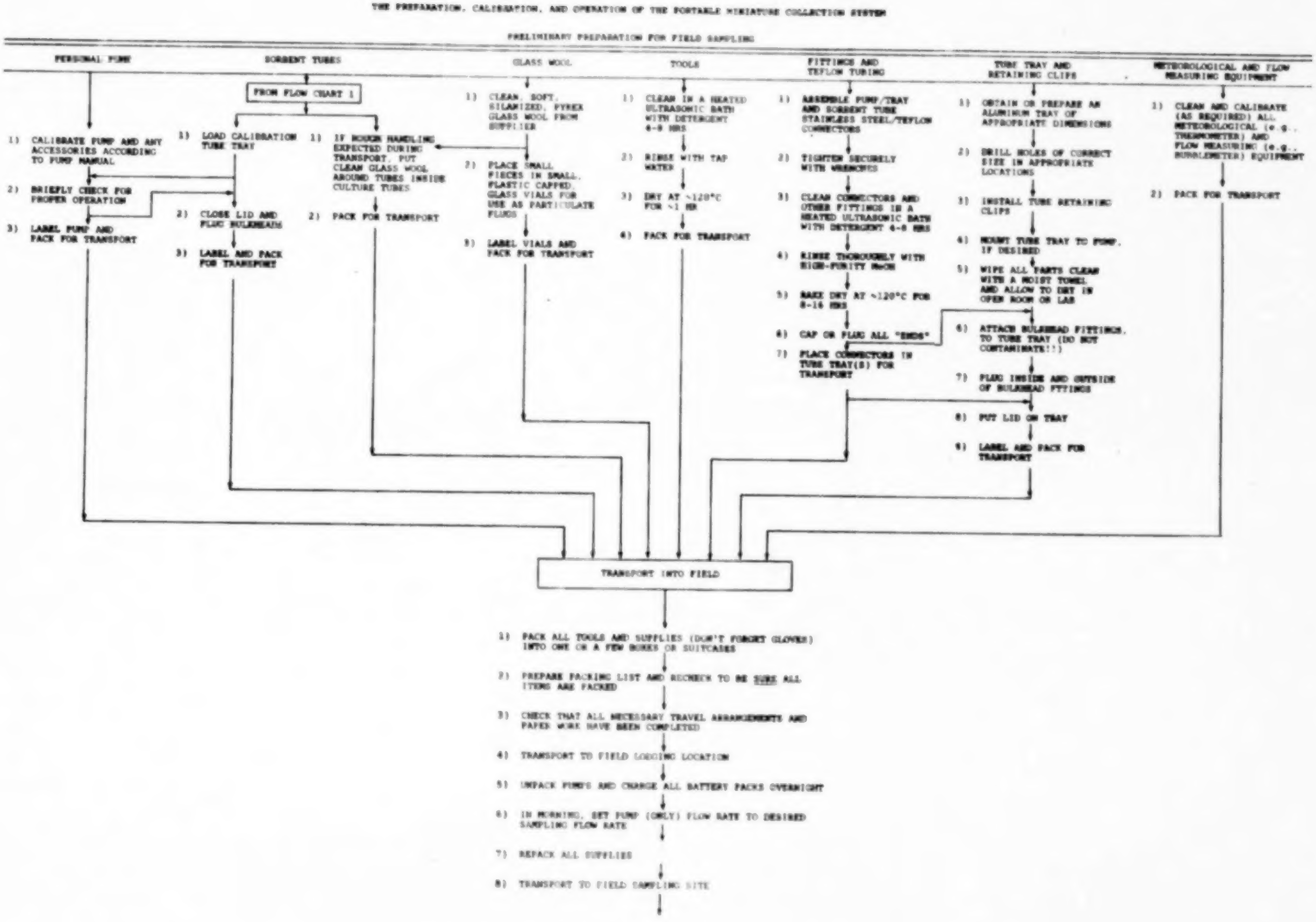
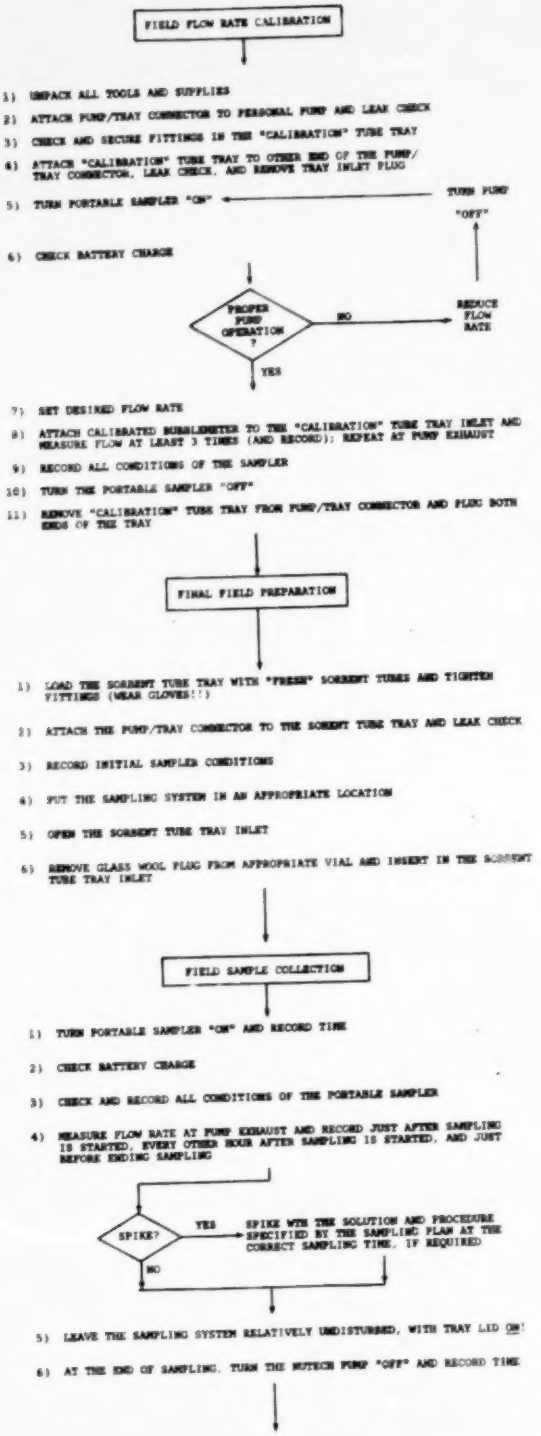

THE PREPARATION, CALIBRATION, AND OPERATION OF THE PORTABLE MINIATURE COLLECTION SYSTEM
PRELIMINARY PREPARATION FOR FIELD SAMPLING
PERSONAL PUMP
SORBENT TUBES
GLASS WOOL
TOOLS
FITTINGS AND TEFLON TUBING
TUBE TRAY AND RETAINING CLIPS
METEOROLOGICAL AND FLOW MEASURING EQUIPMENT
1) CALIBRATE PUMP AND ANY ACCESSORIES ACCORDING TO PUMP MANUAL
2) BRIEFLY CHECK FOR PROPER OPERATION
3) LABEL PUMP AND PACK FOR TRANSPORT
FROM FLOW CHART I
1) LOAD CALIBRATION TUBE TRAY
2) CLOSE LID AND PLUG BULKHEADS
3) LABEL AND PACK FOR TRANSPORT
1) IF ROUGH HANDLING EXPECTED DURING TRANSPORT, PUT CLEAN GLASS WOOL AROUND TUBES INSIDE CULTURE TUBES
2) PACK FOR TRANSPORT
1) CLEAN, SOFT, SILANIZED, PYREX GLASS WOOL FROM SUPPLIER
2) PLACE SMALL PIECES IN SMALL, PLASTIC CAPPED, GLASS VIALS FOR USE AS PARTICULATE PLUGS
3) LABEL VIALS AND PACK FOR TRANSPORT
1) CLEAN IN A HEATED ULTRASONIC BATH WITH DETERGENT 4-8 HRS
2) RINSE WITH TAP WATER
3) DRY AT ~120°C FOR ~1 HR
4) PACK FOR TRANSPORT
1) ASSEMBLE PUMP/TRAY AND SORBENT TUBE STAINLESS STEEL/TEFLON CONNECTORS
2) TIGHTEN SECURELY WITH WRENCHES
3) CLEAN CONNECTORS AND OTHER FITTINGS IN A HEATED ULTRASONIC BATH WITH DETERGENT 4-8 HRS
4) RINSE THOROUGHLY WITH HIGH-PURITY MeOH
5) BAKE DRY AT ~120°C FOR 8-16 HRS
6) CAP OR PLUG ALL "ENDS"
7) PLACE CONNECTORS IN TUBE TRAY(S) FOR TRANSPORT
1) OBTAIN OR PREPARE AN ALUMINUM TRAY OF APPROPRIATE DIMENSIONS
2) DRILL HOLES OF CORRECT SIZE IN APPROPRIATE LOCATIONS
3) INSTALL TUBE RETAINING CLIPS
4) MOUNT TUBE TRAY TO PUMP, IF DESIRED
5) WIPE ALL PARTS CLEAN WITH A MOIST TOWEL AND ALLOW TO DRY IN OPEN ROOM OR LAB
6) ATTACH BULKHEAD FITTINGS, TO TUBE TRAY (DO NOT CONTAMINATE!!)
7) PLUG INSIDE AND OUTSIDE OF BULKHEAD FITTINGS
8) PUT LID ON TRAY
9) LABEL AND PACK FOR TRANSPORT
1) CLEAN AND CALIBRATE (AS REQUIRED) ALL METEOROLOGICAL (e.g., THERMOMETER) AND FLOW MEASURING (e.g., BUBBLEMETER) EQUIPMENT
2) PACK FOR TRANSPORT
TRANSPORT INTO FIELD
1) PACK ALL TOOLS AND SUPPLIES (DON'T FORGET GLOVES) INTO ONE OR A FEW BOXES OR SUITCASES
2) PREPARE PACKING LIST AND RECHECK TO BE SURE ALL ITEMS ARE PACKED
3) CHECK THAT ALL NECESSARY TRAVEL ARRANGEMENTS AND PAPER WORK HAVE BEEN COMPLETED
4) TRANSPORT TO FIELD LODGING LOCATION
5) UNPACK PUMPS AND CHARGE ALL BATTERY PACKS OVERNIGHT
6) IN MORNING, SET PUMP (ONLY) FLOW RATE TO DESIRED SAMPLING FLOW RATE
7) REPACK ALL SUPPLIES
8) TRANSPORT TO FIELD SAMPLING SITE

Figure A-28. Flow Chart II.



1) UNPACK ALL TOOLS AND SUPPLIES
2) ATTACH PUMP/TRAY CONNECTOR TO PERSONAL PUMP AND LEAK CHECK
3) CHECK AND SECURE FITTINGS IN THE "CALIBRATION" TUBE TRAY
4) ATTACH "CALIBRATION" TUBE TRAY TO OTHER END OF THE PUMP/TRAY CONNECTOR, LEAK CHECK, AND REMOVE TRAY INLET PLUG
5) TURN PORTABLE SAMPLER "ON"
6) CHECK BATTERY CHARGE

7) SET DESIRED FLOW RATE
8) ATTACH CALIBRATED BUBBLEMETER TO THE "CALIBRATION" TUBE TRAY INLET AND MEASURE FLOW AT LEAST 3 TIMES (AND RECORD); REPEAT AT PUMP EXHAUST
9) RECORD ALL CONDITIONS OF THE SAMPLER
10) TURN THE PORTABLE SAMPLER "OFF"
11) REMOVE "CALIBRATION" TUBE TRAY FROM PUMP/TRAY CONNECTOR AND PLUG BOTH ENDS OF THE TRAY

1) LOAD THE SORBENT TUBE TRAY WITH "FRESH" SORBENT TUBES AND TIGHTEN FITTINGS (WEAR GLOVES!!)
2) ATTACH THE PUMP/TRAY CONNECTOR TO THE SORBENT TUBE TRAY AND LEAK CHECK
3) RECORD INITIAL SAMPLER CONDITIONS
4) PUT THE SAMPLING SYSTEM IN AN APPROPRIATE LOCATION
5) OPEN THE SORBENT TUBE TRAY INLET
6) REMOVE GLASS WOOL PLUG FROM APPROPRIATE VIAL AND INSERT IN THE SORBENT TUBE TRAY INLET

1) TURN PORTABLE SAMPLER "ON" AND RECORD TIME
2) CHECK BATTERY CHARGE
3) CHECK AND RECORD ALL CONDITIONS OF THE PORTABLE SAMPLER
4) MEASURE FLOW RATE AT PUMP EXHAUST AND RECORD JUST AFTER SAMPLING IS STARTED, EVERY OTHER HOUR AFTER SAMPLING IS STARTED, AND JUST BEFORE ENDING SAMPLING

SPIKE WTH THE SOLUTION AND PROCEDURE SPECIFIED BY THE SAMPLING PLAN AT THE CORRECT SAMPLING TIME, IF REQUIRED

5) LEAVE THE SAMPLING SYSTEM RELATIVELY UNDISTURBED, WITH TRAY LID ON!
6) AT THE END OF SAMPLING, TURN THE NUTECH PUMP "OFF" AND RECORD TIME

Figure A-28 (continued)

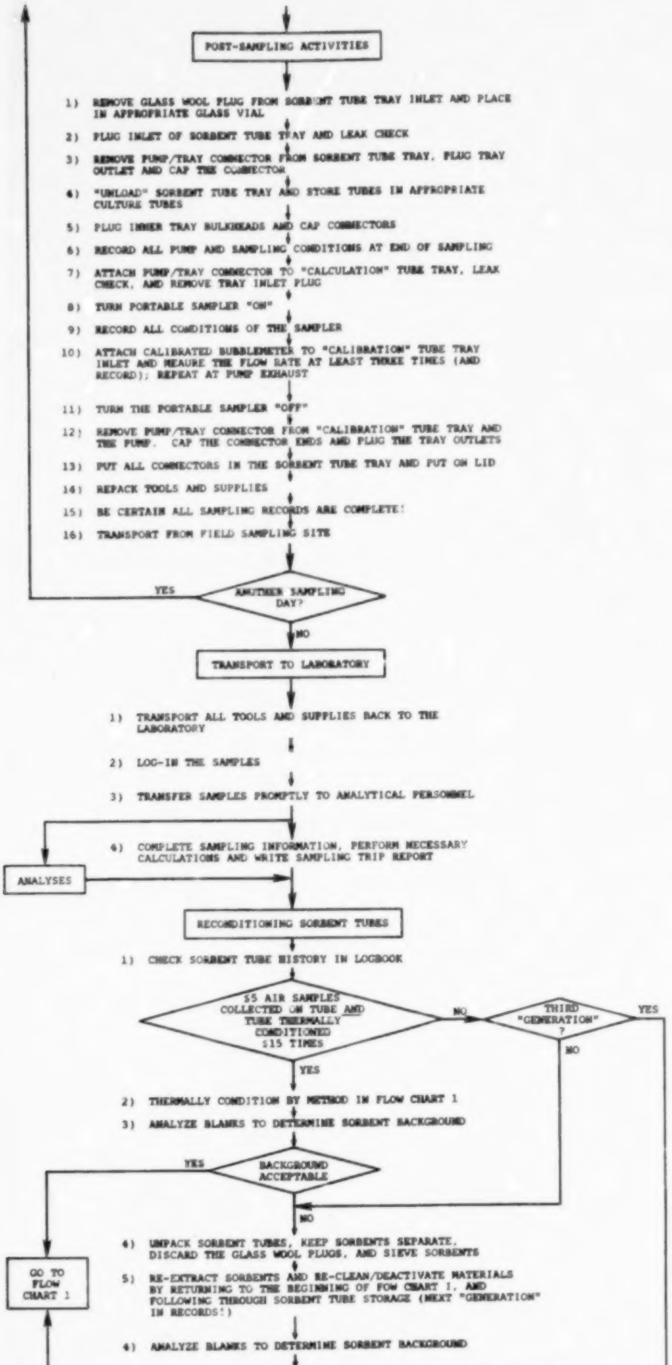

POST-SAMPLING ACTIVITIES
1) REMOVE GLASS WOOL PLUG FROM SORBENT TUBE TRAY INLET AND PLACE IN APPROPRIATE GLASS VIAL
2) PLUG INLET OF SORBENT TUBE TRAY AND LEAK CHECK
3) REMOVE PUMP/TRAY CONNECTOR FROM SORBENT TUBE TRAY, PLUG TRAY OUTLET AND CAP THE CONNECTOR
4) "UNLOAD" SORBENT TUBE TRAY AND STORE TUBES IN APPROPRIATE CULTURE TUBES
5) PLUG INNER TRAY BULKHEADS AND CAP CONNECTORS
6) RECORD ALL PUMP AND SAMPLING CONDITIONS AT END OF SAMPLING
7) ATTACH PUMP/TRAY CONNECTOR TO "CALCULATION" TUBE TRAY, LEAK CHECK, AND REMOVE TRAY INLET PLUG
8) TURN PORTABLE SAMPLER "ON"
9) RECORD ALL CONDITIONS OF THE SAMPLER
10) ATTACH CALIBRATED BUBBLEMETER TO "CALIBRATION" TUBE TRAY INLET AND MEAURE THE FLOW RATE AT LEAST THREE TIMES (AND RECORD); REPEAT AT PUMP EXHAUST
11) TURN THE PORTABLE SAMPLER "OFF"
12) REMOVE PUMP/TRAY CONNECTOR FROM "CALIBRATION" TUBE TRAY AND THE PUMP. CAP THE CONNECTOR ENDS AND PLUG THE TRAY OUTLETS
13) PUT ALL CONNECTORS IN THE SORBENT TUBE TRAY AND PUT ON LID
14) REPACK TOOLS AND SUPPLIES
15) BE CERTAIN ALL SAMPLING RECORDS ARE COMPLETE!
16) TRANSPORT FROM FIELD SAMPLING SITE
YES
ANOTHER SAMPLING DAY?
NO
TRANSPORT TO LABORATORY
1) TRANSPORT ALL TOOLS AND SUPPLIES BACK TO THE LABORATORY
2) LOG-IN THE SAMPLES
3) TRANSFER SAMPLES PROMPTLY TO ANALYTICAL PERSONNEL
4) COMPLETE SAMPLING INFORMATION, PERFORM NECESSARY CALCULATIONS AND WRITE SAMPLING TRIP REPORT
ANALYSES
RECONDITIONING SORBENT TUBES
1) CHECK SORBENT TUBE HISTORY IN LOGBOOK
≤5 AIR SAMPLES COLLECTED ON TUBE AND TUBE THERMALLY CONDITIONED ≤15 TIMES
NO
THIRD "GENERATION" ?
YES
NO
YES
2) THERMALLY CONDITION BY METHOD IN FLOW CHART 1
3) ANALYZE BLANKS TO DETERMINE SORBENT BACKGROUND
YES
BACKGROUND ACCEPTABLE
NO
4) UNPACK SORBENT TUBES, KEEP SORBENTS SEPARATE, DISCARD THE GLASS WOOL PLUGS, AND SIEVE SORBENTS
GO TO FLOW CHART 1
5) RE-EXTRACT SORBENTS AND RE-CLEAN/DEACTIVATE MATERIALS BY RETURNING TO THE BEGINNING OF FOW CHART I, AND FOLLOWING THROUGH SORBENT TUBE STORAGE (NEXT "GENERATION" IN RECORDS!)
4) ANALYZE BLANKS TO DETERMINE SORBENT BACKGROUND
YES
BACKGROUND ACCEPTABLE
NO
DISCARD SORBENTS (BUT SAVE HARDWARE)

Figure A-28 (continued)

APPENDIX B

STANDARD SAMPLE GENERATION SYSTEM

OBJECTIVE

In order to evaluate the sorbent sampling systems used in this project, it was necessary to have a method for generating known concentrations of organic compounds in dynamic gas streams. MRC has developed a dynamic standard Sample Generation System based on the controlled syringe injection of organic liquids into a flowing stream of gas (N_2), vaporization, and subsequent dilution.

INSTRUMENT

The Sample Generation System is shown schematically in Figure B-1. The main frame of the system is a modified gas chromatograph (F&M Model 700) with its protective metal covering and detector removed. The oven [30 cm (12 in.) x 30 cm (12 in.)] is in a relocated position on the left side of the main frame. Of the four heated zones available on the original GC, one controls the oven temperature, two are used to separately control the temperature of the two three-port injection blocks, and the final zone is available for heating transfer lines used for direct interfacing with a detector in frontal analysis capacity studies. A pyrometer (Simpson 0-500°C), a selection switch, thermocouples, and necessary circuit modifications allow the monitoring of temperatures in the four zones.

An aluminum plate [45.7 cm (18 in.) x 46.4 cm (18 1/4 in.) x 0.6 cm (1/4 in.)] is attached to the main frame to the right of the oven to accommodate the syringe drives. Necessary bulk-head fittings, tees, toggle valves, needle valves, tubing, pressure gauges, and rotameters are used in the configuration indicated in the figure. Materials of construction for the flow system are either stainless steel or nickel, and the entire system is contained in a large exhaust hood [2.4 m (8 ft) x 1.2 m (4 ft) x 1.5 m (5 ft)] with front and rear access through double sliding doors. Flow control/sensing instrumentation, pressure gauges, and rotameters are mounted on a panel and rack assembly in the hood above the generation system.

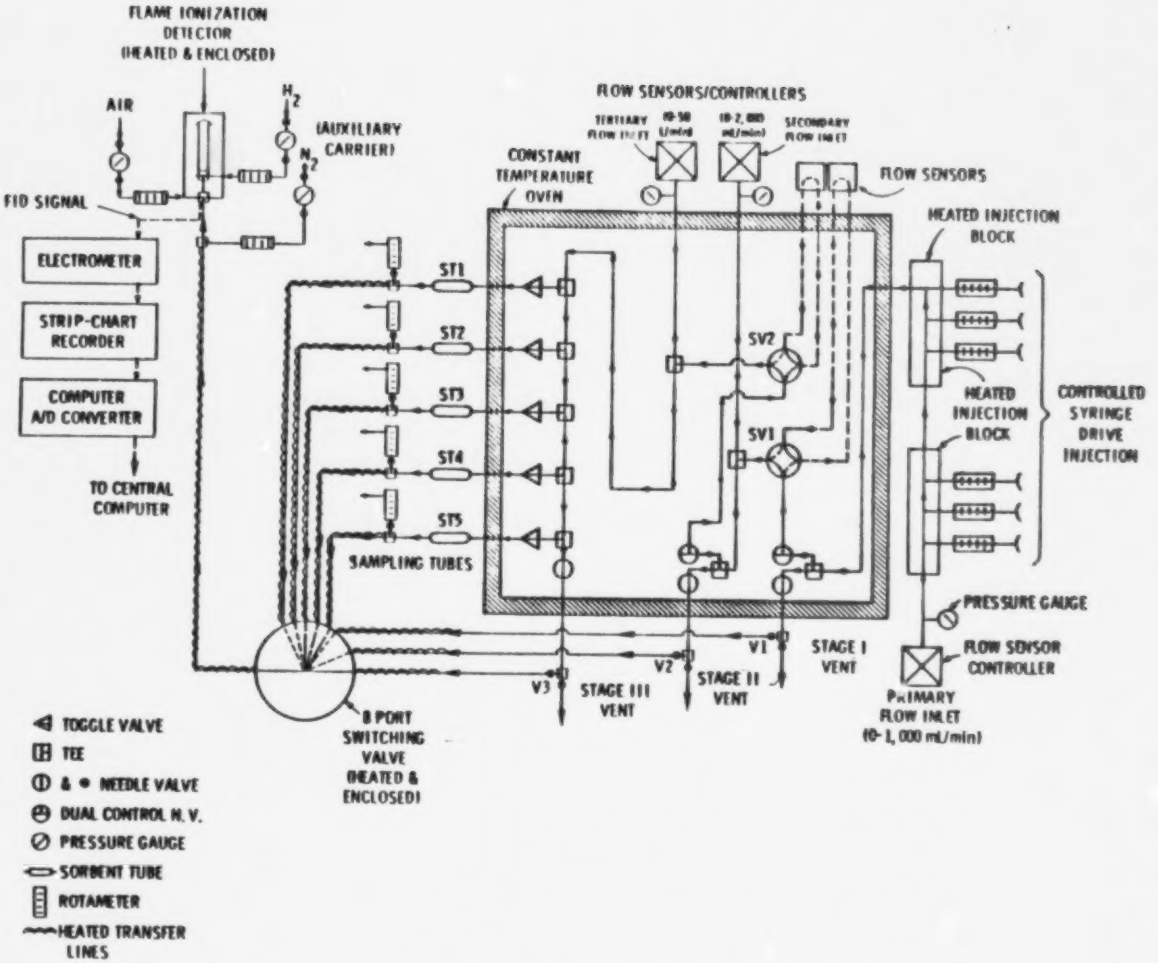

FLAME IONIZATION DETECTOR (HEATED & ENCLOSED)
AIR
H_2
N_2
(AUXILIARY CARRIER)
FID SIGNAL
ELECTROMETER
STRIP-CHART RECORDER
COMPUTER A/D CONVERTER
TO CENTRAL COMPUTER
FLOW SENSORS/CONTROLLERS
TERTIARY FLOW INLET
(0-50 L/min)
(0-2,000 mL/min)
SECONDARY FLOW INLET
CONSTANT TEMPERATURE OVEN
FLOW SENSORS
HEATED INJECTION BLOCK
HEATED INJECTION BLOCK
CONTROLLED SYRINGE DRIVE INJECTION
ST1
ST2
ST3
ST4
ST5
SAMPLING TUBES
SV2
SV1
PRESSURE GAUGE
FLOW SENSOR CONTROLLER
PRIMARY FLOW INLET (0-1,000 mL/min)
V1
STAGE I VENT
V2
STAGE II VENT
V3
STAGE III VENT
8 PORT SWITCHING VALVE (HEATED & ENCLOSED)
TOGGLE VALVE
TEE
& • NEEDLE VALVE
DUAL CONTROL N.V.
PRESSURE GAUGE
SORBENT TUBE
ROTAMETER
HEATED TRANSFER LINES

Figure B-1. Standard Sample Generation System (SGS) with effluent monitor modification.

The Generation System functions in the following manner. A source of carrier gas (N_2) is introduced into the system and split into primary, secondary and tertiary flows. The primary flow passes through a mass-flow sensor/controller (Brooks Model 5841) which maintains the flow rate at a preset value (0-1,000 mL/min). This flow passes through individually heated and controlled injection blocks which are each designed to accept three syringes mounted on variable-control syringe drives (Sage Model 355). This permits the simultaneous introduction of six pure liquid components, or potentially many more, if mixtures of compounds are used in the syringes. The rate of injection can be varied from submicroliter/hour to milliliter/minute by the appropriate choice of syringe size and drive rate. Liquid samples are vaporized in the injection blocks and swept with the carrier gas into a constant temperature oven.

Most of the primary flow passes through the oven and through a needle valve used to regulate the pressure in the primary flow path. It is then expelled to the vent (V1). A small portion (usually ~10 mL/min) of the primary flow is removed through a dual-control needle valve and passes into a switching valve (SV1) which is actually one-half of an eight-port switching valve. The second half of the switching valve is used for an identical function in the second dilution stage. The switching valve makes it possible to insert a mass-flow sensor (Brooks Model 5810, 0-100 mL/min) in the flow path (indicated by the dashed line in Figure B-1) to measure the exact split of the primary flow. Once the split has been established, the flow sensor is switched out of the system so that the sensing elements are not subjected to sample-containing organic vapors. The split is maintained by carefully controlling the pressures in each dilution stage.

Pressures are monitored with precision pressure gauges [Heise Model CM, 0-6.9 x 10^5 Pa (0-100 psi)]. By maintaining a constant pressure in each dilution stage, a constant pressure differential is established between the stages assuring a consistent split ratio across the needle valves.

The split-out portion of the primary flow passes from the switching valve and is combined with the secondary carrier flow which enters the constant temperature oven through a mass-flow sensor/controller (Brooks Model 4841, 0-2,000 mL/min). As in the case of the primary flow, most of the secondary flow passes through the oven and is expelled to the vent (V2) through a needle valve. A small portion (usually 10 mL/min) of the secondary flow is removed through a dual-control needle valve and passes into a switching valve (SV2). This valve functions in an identical manner to SV1 and places a second mass-flow sensor (Brooks, Model 5810, 0-100 mL/min) in the flow path for measuring the second split.

The split-out portion of the secondary flow passes from the switching valve and is combined with the final (tertiary) dilution stream which enters the constant temperature oven through a mass-flow sensor/controller (Brooks Model 5841, 0-50 L/min). This final concentration is available for sampling through a five-port manifold system that will accommodate sorbent sampling tubes. Sampling rates through the sorbent tubes are maintained by rotameters (Brooks Model 1110) at the tube exits. The unused portion of the final dilution stage is expelled to the vent (V3).

The sample generation system is connected through an eight-port (Valco) selection valve and stainless-steel tubing [1.6 mm (1/16 in.)] to a flame ionization detector. This arrangement permits the selective monitoring of concentration levels in each of the three dilution stages and the additional monitoring of effluent from five sampling locations.

Evaluation studies have demonstrated linear concentration responses over the operational ranges of the syringe drive rate, the two split monitors, and the three dilution stages. By the appropriate selection of syringe size, drive rate, split ratios, and dilution rates, it is possible to achieve continuously variable concentrations from percent to low part-per-trillion levels using this system.